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U. S. Department of Commerce
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Experimental Manufacture of Paper for War Maps

By Charles G. Weber and Merle B. Shaw [1]

Early in World War II, a new map paper was developed that greatly improved the quality and performance of war maps. The National Bureau of Standards cooperated in the development and, subsequently, determined by experimental manufacture how to make the paper from commercially available raw materials. The best results were obtained in experimental manufacture by using fiber furnishes of 100-percent strong bleached sulfate pulps with the addition of melamine-formaldehyde resin to increase the wet strength and titanium dioxide to produce the desired capacity. It was essential that the beating be very carefully controlled to preserve the maximum fiber strength. The most critical requirements from a manufacturing standpoint were very high resistance to tear, high wet tensile strength, high opacity, and good smoothness. A moderate degree of wildness was not objectionable. The data obtained by experiments were applied to initiate the commercial production of the new paper to meet unprecedented tonnage requirements.

I. Introduction

The Paper Section of the National Bureau of Standards cooperated actively with the Army Map Service of the Corps of Engineers in the development of a new type of map paper that proved highly important during World War II. Unique qualities built into this paper gave satisfactory performance in contact with the water, mud, and grime of the battlefield that had disintegrated papers heretofore used. This Bureau assisted in bringing the new type of paper into commerical production after its merits were established. Information essential to this step was obtained through semicommercial paper-making experiments. A detailed specification [2] for the paper was formulated at the Army Map Service with the cooperation of the Bureau. The most important feature of the paper was its high wet strength which was obtained by the relatively new development of resin bonding.[3 4 5]

The requirements of the specification were very

[1] Other members of the Paper Section contributed to this work. Particular acknowledgment is made to Martin J. O'Leary and Joshua Missimer for assistance in the papermaking, and to Thelma L. O'Brian, William K. Wilson, Irma G. Callomon and Alice J. Padgett for testing the samples.

[2] Specification No. 43-142, Army Map Service, Wash., D. C.

[3] C. G. Weber, Notes on resin-bonded, wet-strength papers, Printing Equip. Eng. **70**, No. 5: 38 (Aug. 1945).

[4] Geo. E. From, Melamine resins for development of wet and dry strengths of paper, Pulp & Paper Mag. (Canada) **46**, No. 3: 157 (March 1945).

[5] Ralph W. Kumler, Melamine resins in industry, So. Pulp & Paper J. **19**, No. 5: 20 (May 1946).

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stringent. They demanded the rugged strength when dry, wet, or oil-soaked that gave the maps their durability. In addition, they called for low expansivity; high opacity when wet, dry, or oiled; good writing quality when wet or dry; low acidity; and smoothness suitable for printing multicolor line maps and 200-line photomaps. Close limitations were placed on thickness, weight, and moisture content. The paper-making experiments determined how the paper could be made from available raw materials to meet the specification.

The information obtained was applied with much success in assisting commercial mills to get into successful production of the paper with a minimum of delay. It was of great value also as basis for judging from the properties of papers meeting all details of the specification, changes composition or manufacturing technique necessary to bring the papers up to standard.

When it became important to explore the possibilities of saving space and weight in the shipment of maps by air, the results were especially useful. With the data at hand, it was possible for the Paper Section to produce quickly, quantities sufficient for printing trial lots of maps papers embodying optimum qualities obtainable in lighter weights. The maps from these printings were used by the Army Engineers to establish the utility and durability of lightweight maps.

II. Experimental Paper-making Equipment

The equipment of the Bureau's paper mill is semicommercial in size, and is adapted to the experimental manufacture of papers under conditions which simulate those of industrial plants. Detailed descriptions and photographs of the equipment are contained in previous publications.[6,7,8] The equipment used in this particular work consisted essentially of a 50-pound beater with copper-lined wooden tub and manganese-bronze bars and plate; a jordan refiner with bars of bronze and steel alloy; a four-plate, flat screen; a 29-inch Fourdrinier paper-making machine with a wire 33 feet long, two presses, nine 15-inch dryers, a machine calender stack of 7 rolls, and reel; and a five-roll supercalender.

[6] M. B. Shaw and G. W. Bicking. Caroa fiber as a papermaking material. Tech. Pap BS 21, 338 (1927) T340.

[7] M. B. Shaw and G. W. Bicking. Further experimental production of currency paper in the Bureau of Standards paper mill, BS J. Research 904 (1929) RP 121.

[8] M. B. Shaw. Equipment and research work of the Bureau of Standards paper mill, Paper Trade J. 89, No. 19, 60 (1929).

III. Fibrous Raw Materials

The extremely high strength required for the map paper made it essential that all or a large proportion of the fibers used be of high strength. Rag fibers were not given consideration because neither an adequate supply of rags nor sufficient rag-cooking equipment was available to meet anticipated needs. Hence, the experiments were confined to commercially available bleached wood pulps. The following pulps were used either singly or in mixture:

1. Northern bleached sulfate, made by cooking eastern spruce in a strong solution containing caustic soda and sodium sulfide. This was very strong, long-fibered wood pulp.

2. Bleached sulfate No. 2 made from mixed species of relatively poor wood. This was somewhat like No. 1, but softer and weaker because of the lack of adequately selected woods at the producing mill.

3. Western bleached sulfate, a very strong wood pulp made from western hemlock. It was comparable to No. 1 in quality.

4. Bleached sulfite, made by cooking eastern spruce wood in a solution of calcium bisulfite. This was a standard quality of pulp used for bond papers. It was a relatively long-fibered, strong pulp, but not as strong as the sulfate-cooked pulps made from selected woods.

5. Deciduous wood soda, a filler pulp produced by cooking wood in a strong solution of caustic soda. This was an unusually strong soda pulp. However, no pulp of this type is comparable to the sulfate or coniferous sulfite pulps in strength or length of fibers. Its use in a paper contributes to

printing quality and formation of paper rather than to the strength.

6. Deciduous wood sulfite, a short-fibered filler pulp made by cooking deciduous woods in a solution of calcium bisulfite. It was comparable to soda pulp in most of its characteristics.

The chemical characteristics of these pulps are shown in table 1.

TABLE 1.—*Chemical characteristics of fibrous materials used in experimental manufacture of war-map papers*

Pulp	Alpha-cellulose content[1]	Beta-cellulose content[1]	Gamma-cellulose content[1]	Pento-sans	Copper number	Ash[2]	Resin[2]	Acidity of pulp (glass-electrode method)	
								Cold-water extraction	Hot-water extraction
	%	%	%	%		%	%	pH	pH
"Northern" bleached sulfate	85.4	8.6	6.0	6.5	0.7	0.1	0.1	5.8	5.3
No. 2 bleached sulfate	83.8	10.2	6.0	8.1	1.9	.3	.1	6.1	5.5
"Western" bleached sulfate	86.3	6.3	7.4	5.2	.9	.2	.1	6.7	6.2
Coniferous wood sulfite	84.4	3.6	12.0	4.2	1.3	.2	.4	5.8	5.5
Deciduous wood soda	84.6	13.1	2.3	15.3	1.3	3.0	.4	4.2	3.6
Deciduous wood sulfite	83.6	10.9	5.5	6.0	1.0	.2	.1	6.9	6.2

[1] Based on total cellulose.
[2] On oven-dry basis.

IV. Manufacturing Procedure

Before the furnish was added to the beater, the roll was raised off the plate a definite number of turns. The position of the beater roll is expressed as the number of turns above (+) or below (−) zero setting, which is the point of contact between the roll and the bedplate. One turn moves the roll 0.008 inch. The various positions of the roll and the time intervals for each during the beating of a furnish are shown in figure 1.

Forty-eight pounds of pulp was furnished to the beater in each instance. The pigment, titanium dioxide, was added during the furnishing. After the furnishing, which took about 15 minutes, the beater roll was gradually lowered by definite steps at fixed intervals throughout the beating, as indicated by the beating curve in figure 1. The rosin size was added 1 hour, and the alum (aluminum sulfate) ½ hour, before completion of the beating cycle.

The beaten stock was dropped to a chest and pumped in a continuous stream through the stuff box and the jordan to the paper machine without the use of a machine chest. The stuff box was of the familiar regulating type, having a constant head over an adjustable orifice. Screen plates with 0.018-inch slots were used for all runs. The jordan was used as a mixer only, on the same setting for all runs.

When melamine-formaldehyde resin was used it was added as a colloidal solution made by dissolving the resin in the form of a fine white powder

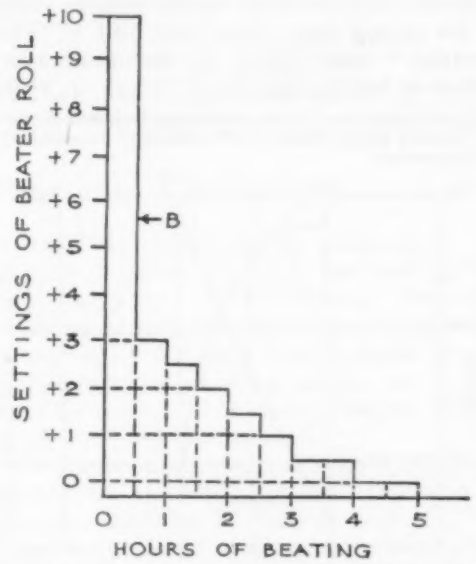

FIGURE 1.—*Standard practice of lowering the beater roll for all experimental map papers.*

"*B*", Pattern of beating curve for all papers. Value for roll settings are turns of the handwheel above (+) contact (0) of roll with bedplate. One turn moves the roll 0.008 inch. Lighter bar down at start.

in warm water acidified with hydrochloric acid. The solution was added continuously to the stock leaving the screen, just before it entered the head box of the paper machine. The stock was uniformly mixed by baffles in the head box, and the temperature of the stock was maintained at 90° ±2° F at that point.

Rosin size was used in all papers. It was precipitated with papermakers alum, $Al_2(SO_4)_3$, which was used to control the pH of the stock. The papers were opacified with titanium dioxide. The finish imparted by the small machine calender was insufficient, and it was necessary to improve the smoothness by light supercalendering.

V. Testing

All physical and chemical tests of the pulps and papers referred to in this article were made in accordance with the official methods [9] of the Technical Association of the Pulp and Paper Industry. Wet bursting strength and wet tensile strength were determined on samples immediately after immersion for 1 hour in water at 73° F, using the same procedure as for corresponding tests on samples conditioned in the normal manner. The pH of mill waters at the beater, stuff box, and head box was determined electrometrically, using a quinhydrone electrode.

[9] Copies of the Methods available from the Association at 122 E. Forty-Second Street, New York 17, N. Y.

VI. Results

The first papers were made of all eastern sulfate. It was the strongest bleached commercial wood pulp available at the time, and the first problem was to determine how to make the best possible paper from it. By making a series of papers, varying one factor at a time, it was established that the most suitable map paper produced was made with only 3 hours of beating with the jordan set for mixing only. The sheet had a "wild" formation [10] when judged by the time-honored method of looking through it. However, visible formation *per se* was of no importance, and no reference was made to it in the specification. Tearing strength and wet tensile strength in the cross direction were the most critical properties from the control standpoint. More than 3 hours of beating resulted in low tearing strength and correspondingly high expansion. This relationship is shown graphically in figure 2. This control of beating was absolutely essential to the production of a paper with satisfactorily high resistance to tear and low distortion.

[10] A paper is said to have wild formation when the fibers are so distributed as to present a mottled, streaked, or "curdled-milk" appearance when viewed against light.

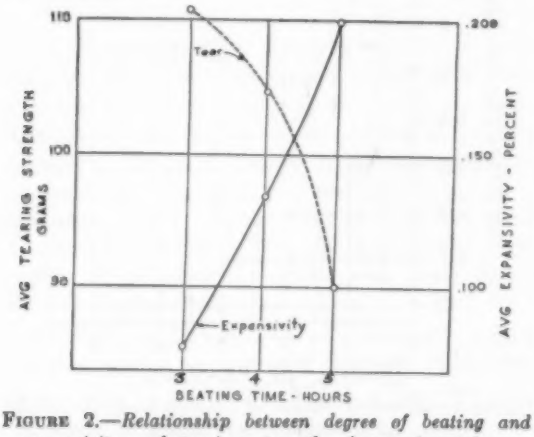

FIGURE 2.—*Relationship between degree of beating and expansivity and tearing strength of experimental map papers.*

High wet strength and important increase in the dry or normal strength was obtained by using melamine-formaldehyde resin. Three percent was required to obtain the necessary wet strength, and more than 3 percent reduced the resistance to tear rather sharply by a continuous film effect.

Some difficulty was encountered in obtaining reasonably high retention of the opacifying pigment when the melamine resin was first used. A control paper without this resin, with 3 percent of titanium dioxide added, had an opacity value of 93 percent. The next paper made was a duplicate, except that 3 percent of melamine resin was added. Less alum was required to adjust the pH because the resin solution added was strongly acid. Poor retention of pigment resulted, and the opacity dropped to 86 percent. The loss of pigment was found to be caused by a deficiency of alumina present from hydrolysis of the alum. It was corrected by adding an excess of alum and then adjusting the pH

ith sodium carbonate. Apparently, the impor-nt role in holding the particles of pigment to e fibers is played by positively charged alumina, hich acts as an electrostatic cement between the bers and the pigment, each of which carry nega-re charges. The use of sodium phosphoalumi-ate as a source of alumina, which does not reduce H, had little effect on retention. However, by dding an excess of alum, excellent opacity was gain obtained. Thereafter, 3 percent of alum, lus sufficient sodium carbonate to give a pH of .5 at the head box, was used in all instances. hese results are in complete agreement with the ublished findings of Martin and Willets [11] regard-ng the influence of the positively charged alumina n the retention of fillers in paper.

It was found possible to meet all of the require-ments of the specification by use of 100 percent of ither eastern sulfate or western sulfate. How-ver, attempts to obtain satisfactory strength hen using the sulfate made from mixed species f wood of poor quality were unsuccessful. Apparently the presence of short, soft fibers from eciduous woods reduced the fiber strength below he minimum required for this quality of paper. Figure 3 shows a comparison of some of the most important properties of the best papers that could be made by using various fiber furnishes. At-tempts to extend the strong, and somewhat critical, sulfate pulps by the addition of filler pulps were only partially successful. The addition of as little as 12½ percent of deciduous wood sulfite or soda, both high-grade filler pulps, resulted in failure to meet the specification in some respects. Even coniferous sulfite, which is a relatively strong wood pulp, could not be used in amounts over about 10 percent without failure to meet the required tearing strength.

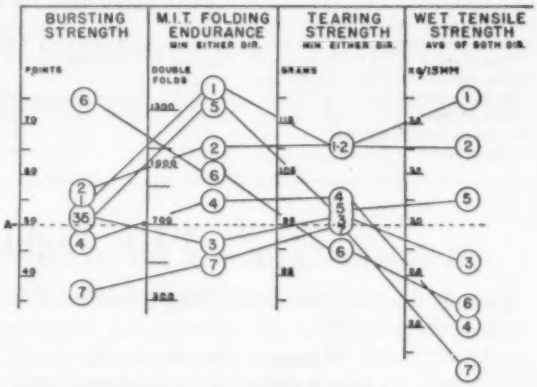

FIGURE 3.—*Relationship between fiber furnish and some strength properties of experimental map papers.*

A, specification level.
1. 100% northern bleached sulfate.
2. 100% western bleached sulfate.
3. 87½% northern bleached sulfate, 12½% deciduous sulfite.
4. 87½% northern bleached sulfate, 12½% strong soda.
5. 90% northern bleached sulfate, 10% bleached sulfite.
6. 70% northern bleached sulfate, 30% bleached sulfite.
7. 100% sulfate from mixed species.

The beating time for all papers was 3 hours. 3% melamine resin added.

[11] S. W. Martin and W. R. Willets, Retention of fillers, Tech. Assn. Papers, Series XXIII, No. 1, 264 (1940). Tech. Assn. of the Pulp & Paper Ind.

VII. Application to Commercial Production

With the information developed in the experimental work, it was possible to give maximum assistance in extending the commercial manufacture of the paper to widely distributed mills to meet quickly the unprecedented needs of the armed forces. Technical service was provided for mills on their initial orders and more than a dozen mills were able quickly to make paper meeting the very high standards of the armed forces. Table 2 contains pertinent data on the properties of nine map papers made early in the program at widely distributed commercial mills. All these mills followed specific technical instructions from the Bureau based on information obtained in the experimental work. The success in applying the information is shown by the consistent manner in which the various papers conformed to, and in many instances exceeded, the most difficult requirements of the specification. Production exceeding 10,000,000 pounds per month within approximately 6 months after initiation of commercial manufacture of an entirely new type of paper was accomplished with a minimum of delay or loss of critical raw materials.

That these papers were well made is attested by the following statement in a letter of commendation from the Office of Chief of Engineers, War Department, "Millions of maps have been printed on this high wet-strength paper, and their superior durable qualities have proved eminently satisfactory to troops in all theaters of war."

TABLE 2.—*Test data on commercial, wet-strength map papers from nine different mills of wide geographic distribution*

Property	Manufacturer									Specification requirements
	A	B	C	D	E	F	G	H	I	
Weight, 17X22: 1,000, lb	49.0	47.7	48.7	49.2	49.1	48.8	47.7	47.1	46.6	48±10%.
Thickness, inch	0.0043	0.0043	0.0043	0.0045	0.0044	0.0043	0.0043	0.0042	0.0043	0.0040±10 %.
Bursting strength, points	64	55	55	69	55	54	47	51	55	50 minimum.
Bursting strength, wet, points	30	23	24	35	29	29	27	24	24	20 minimum.
Tearing strength, grams:										
Machine direction	95	95	100	103	101	93	106	104	100	95 minimum.
Cross direction	110	107	109	121	130	101	118	122	109	Do.
Tensile strength, wet, kg/15 mm:										
Machine direction	4.4	3.9	3.9	4.5	3.6	3.7	4.4	4.9	3.9	3.5 minimum.
Cross direction	2.9	2.6	2.5	2.9	2.5	2.5	2.6	2.5	2.5	2.5 minimum.
Folding endurance (MIT), double folds:										
Machine direction	1,590	1,070	1,460	1,355	1,040	1,330	1,280	1,240	1,460	700 minimum.
Cross direction	940	805	720	1,295	1,050	1,440	740	770	720	Do.
Smoothness (Bekk), seconds	63	53	46	37	43	42	55	51	46	50 to 100.
Opacity, percent	91	92	93	93	90	90	91	90	93	91 minimum.

VIII. Lightweight Paper

Late in the war, the Army Map Service investigated the possibility of reducing the shipping weight and bulk of maps. To aid in this work, the Bureau made a number of experimental runs and determined the qualities that could be obtained in reduced weights. The Map Service was furnished with sufficient quantities of two experimental papers, 12½ percent and 25 percent below the standard weight, respectively, for printing and performance tests. When the performance of the lighter paper was found to be sufficiently promising to justify commercial-scale purchase, the Paper Section had the data for a detailed specification. This paper was composed of 100 percent northern or western bleached sulfate with 3 percent of melamine resin for wet strength and 3 percent of titanium dioxide pigment for opacity. It was made with absolute minimum of beating to preserve the fiber strength. The resulting tendency to "wildness" in formation did not affect adversely the printing characteristics or appearance of the finished maps.

IX. Summary and Conclusions

The development of the improved paper for war maps and the commercial manufacture of it were accomplished through cooperative effort. The Bureau was particularly active in determining how the paper should be made from available materials for optimum performance.

The best results were obtained in experimental manufacture by using fiber furnishes of 100-percent strong bleached sulfate pulps with melamine-formaldehyde resin for wet strength and titanium dioxide for opacity. It was essential that the beating be very carefully controlled to preserve the maximum fiber strength. The most critical requirements from a manufacturing standpoint were the very high resistance to tear, high wet tensile strength, high opacity, and good smoothness. A moderate degree of wildness was not objectionable.

A lightweight paper was developed that reduced the shipping weight and bulk of maps by 25 percent. It was composed of 100 percent of the strongest bleached fibers with 3 percent of melamine resin and 3 percent of titanium dioxide. It was made with absolute minimum of beating.

WASHINGTON, September 17, 1946.

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Purification, Purity, and Freezing Points of 7 Heptanes, 16 Octanes, 6 Pentenes, Cyclopentene, and 7 C_9H_{12} Alkylbenzenes of the API-Standard and API-NBS Series[1*]

By Anton J. Streiff,[2] Evelyn T. Murphy,[2] Vincent A. Sedlak,[2] Charles B. Willingham, and Frederick D. Rossini

This report describes the purification and determination of freezing points and purity of 37 hydrocarbons of the API-Standard and API-NBS series, including 7 heptanes, 16 octanes, 6 pentenes, cyclopentene, and 7 C_9H_{12} alkylbenzenes.

I. Introduction

A recent report from this laboratory described the purification and determination of freezing points and purity of the first 31 compounds of the API-NBS series of hydrocarbons [1].** Beginning July 1, 1944, the preparation of hydrocarbons of the API-NBS series was greatly accelerated by the cooperative program on standard samples of hydrocarbons operated by the American Petroleum Institute and the National Bureau of Standards.[3]

Under the cooperative program, the target for the final product was 1 liter of API-Standard material with a purity of 99.8 mole percent to be used for standard samples, plus 0.2 liter of material of higher purity for the API-NBS samples, to be made available on loan to qualified investigators for the measurement of needed properties.[4]

*Presented before the Division of Petroleum Chemistry of the American Chemical Society, Chicago, Ill., September 1946.

**Figures in brackets indicate the literature references at the end of this paper.

[1] This investigation was performed at the National Bureau of Standards as part of the work of the American Petroleum Institute Research Project 6 on the Analysis, Purification, and Properties of Hydrocarbons.

[2] Research Associate on the American Petroleum Institute Research Project 6 at the National Bureau of Standards.

[3] This cooperative program on standard samples of hydrocarbons was organized by the then newly formed API Research Project 46 Committee on Hydrocarbons for Spectrometer Calibration (W. J. Sweeney, chairman, L. C. Beard, Jr., T. G. Delbridge, F. E. Frey, H. Gershinowitz, H. Levin, and R. F. Marschner, with H. J. Hall as secretary, and C. E. Boord, M. R. Fenske, F. D. Rossini, and F. C. Whitmore as consultants). This committee was set up by the API Advisory Committee on Fundamental Research on the Composition and Properties of Petroleum (J. Bennett Hill, then chairman) to effect a cooperative program with the National Bureau of Standards whereby there could be brought to bear on the problem of preparing standard samples of hydrocarbons all the facilities of the existing research projects of the Institute so that the provision of finished hydrocarbon standards could be materially speeded up. See references [2 and 3] for further details.

[4] The allocation of these samples is handled by the Advisory Committee for the API Research Project 44 on the "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons" (W. E. Kuhn, chairman, Otto Beeck, Gustav Egloff, and S. S. Kurtz, Jr., with F. D. Rossini as supervisor of the project).

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II. Materials

The starting materials were supplied as follows: [5] By the API Research Project 45 on the "Synthesis and Properties of Hydrocarbons of Low-Molecular Weight" at the Ohio State University, Columbus, Ohio, under the supervision of C. ... Boord: 3-Ethylpentane, 2-methylheptane, 3-methylheptane, 4-methylheptane, 3-ethylhexane, 2,2-dimethylhexane, 2,3-dimethylhexane, 3,3-dimethylhexane, 3,4-dimethylhexane, 2-methyl-3-ethyl...

[5] A letter (*B*) following the name of a compound indicates that, for the API-NBS series, it is a second (and usually slightly purer) sample of the given compound, the first sample of which is labeled (*A*). (See reference [1].)

TABLE 1.—*Information on the purification of 37 API–Standard and API–NBS hydrocarbons*

Compound [a]	Laboratory [b] providing starting material	Hydrocarbon charged for distillation		Distillation [f]								Volume of selected sample
		Volume	Purity	Kind [c]	Azeotrope-forming substance [d]	Amount of hydrocarbon in the azeotropic distillate [e]	Distilling column number [f]	Number of theoretical plates [f] (approx.)	Reflux ratio [f] (approx.)	Rate of collection of distillate	Results plotted in figure	API-Standard
		Liters	*Mole %*			*% by volume*				*ml/hr*		*ml*
PARAFFINS												
2-Methylhexane	Ethyl	0.70		Azeo	Methanol	60	11	(*)	290/1	2.5	3	
		.44		do	Ethanol	64	10	135	145/1	5.0	4	1340
3-Methylhexane	do	1.75 [g]		do	Methanol	60	11	(*)	290/1	2.5	5	
		.81		do	Ethanol	64	7	130	145/1	8.5	6	1160
3-Ethylpentane	APIRP45	2.38 [h]		do	do	65	10	135	145/1	5.0	7	1820
2,2-Dimethylpentane	Socony-Vacuum	2.87		do	do	74	7	130	145/1	8.5	8	2110
2,3-Dimethylpentane	General Motors	3.70	97.94	do	do	64	8	130	145/1	8.5	9	1215
2,4-Dimethylpentane	APIRP6 [i]	3.87		do	do	71	4	200	145/1	5.0	10	1200
3,3-Dimethylpentane	Ethyl	2.00	99.35	do	do	68	9	135	145/1	5.0	11	1020
Do	APIRP45	1.87		do	do	68	7	130	155/1	8.0	12	
n-Octane	APRIP6 [a]	3.15		do	do	68	7	130	155/1	8.0	13	
		6.38	98.78	Reg			13	130	155/1	8.0	13	
2-Methylheptane	APIRP45	2.48	99.75	Azeo	Cell	72	15	125	110/1	14.0	14	1620
3-Methylheptane	do	2.01	96.71	do	Ethanol	41	7	130	145/1	8.5	15	930
		5.87		Reg			14	125	110/1	14.0	16	
		2.99		do			4	200	160/1	4.5	17	
		1.80 [j]		Azeo	Ethanol	39	8	130	145/1	8.5	18	
		1.53	99.46	Reg			4	200	160/1	4.5	19	970
4-Methylheptane	do	2.38	99.73	do			12	135	185/1	4.0	20	
		1.85		Azeo	Ethanol	39	14	125	125/1	12.5	21	1060
3-Ethylhexane	do	5.15		Reg			7	130	145/1	8.5	22	
		3.27		do			10	135	185/1	4.5	23	1150
2,2-Dimethylhexane	do	3.75	98.25	do			15	125	110/1	14.0	24	
		2.70	99.19	Azeo	Ethanol	54	13	130	155/1	8.0	25	920
2,3-Dimethylhexane	APIRP45	2.64		Reg			12	135	165/1	4.5	26	
		1.65		Azeo	Ethanol	45	8	130	155/1	8.0	27	945
2,4-Dimethylhexane	Penn State	3.70		Reg			9	135	145/1	5.0	28	
		3.20		Azeo	Me. Cell	75	7	130	145/1	8.5	29	1206
2,5-Dimethlyhexane	do	3.10	99.30	do	Cell	84	14	125	110/1	14.0	30	1216
3,3-Dimethylhexane	APIRP45	3.40		do	do	83	14	125	110/1	14.0	31	
		2.00		Reg			12	135	185/1	4.0	32	1000
3,4-Dimethylhexane	do	2.40		do			12	135	145/1	5.0	33	
		1.86		Azeo	Ethanol	40	8	130	155/1	8.0	34	860
3-Methyl-3-ethylpentane	do	2.63		Reg			12	135	145/1	5.0	35	
		1.85		do			4	200	160/1	4.5	36	1000
3-Methyl-3-ethylpentane	APIRP45	3.70		Azeo	Cell	76	14	125	110/1	14.0	37	
		3.13		Reg			9	135	165/1	4.5	38	1135
2,2,3-Trimethylpentane	General Motors	12.25	91.4	do			6	125	110/1	14.0	39	
		2.52	99.05	Azeo	Ethanol	47	15	125	125/1	12.5	40	
		1.82	99.40	Reg			4	200	160/1	4.5	41	470 [k]
		3.30 [l]		Azeo	Me. Cell	76	15	125	125/1	12.5	42	1080 [k]
2,3,3-Trimethylpentane	Penn State	3.00	94.2	Reg			9	135	145/1	5.0	43	
		2.23		Azeo	Ethanol	43	8	130	155/1	8.0	44	990
2,3,4-Trimethylpentane	APIRP45	4.17		Reg			7	130	145/1	8.5	45	
		2.58		Azeo	Ethanol	43	14	125	125/1	12.5	46	1370

See footnotes at end of table.

TABLE 1.—*Information on the purification of 37 API–Standard and API–NBS hydrocarbons*—Continued

Compound [a]	Laboratory [b] providing starting material	Hydrocarbon charged for distillation		Distillation [f]								Volume of selected sample	
		Volume	Purity	Kind [c]	Azeotrope-forming substance [d]	Amount of hydrocarbon in the azeotropic distillate [e]	Distilling column number [f]	Number of theoretical plates [f] (approx.)	Reflux ratio [f] (approx.)	Rate of collection of distillate	Results plotted in figure	API-Standard	API-NBS
ALKYLBENZENES													
		Liters	*Mole %*			*% by volume*				*ml/hr*		*ml*	*ml*
n-Propylbenzene (*B*)	APIRP6 [g]	[h] 5.50		Reg.			8	130	125/1	10.0	47		
		[=] 5.15		Azeo.	Cell.	23	5	125	110/1	14.0	48		
		2.12	99.42	Reg.			13	130	200/1	6.0	49	1310	340
1-Methyl-2-ethylbenzene	APIRP45	2.54		do			7	130	145/1	8.5	50		
		1.91		Azeo.	Cell. [i]	8	4	200	145/1	5.0	51	988	250
					Me. Carb.	84							
1-Methyl-3-ethylbenzene	do	2.80		Reg.			8	130	145/1	8.5	52		
		1.20		Azeo.	Me. Carb.	92	8	130	145/1	8.5	53		
		1.00	93.5	do	do	92	9	135	145/1	5.0	54		
		[k] 2.30	93.0										
		1.19	97.26				[l]				55	685	45
1-Methyl-4-ethylbenzene	NACA	2.03	99.60	Azeo.	Me. Carb.	91	12	135	145/1	5.0	56	1145	275
1,2,3-Trimethylbenzene (*B*)	APIRP45	2.03	99.75	do	do	74	10	135	105/1	4.5	57	1025	153
1,2,4-Trimethylbenzene (*B*)	NACA	3.41	99.59	do	do	85	4	200	145/1	5.0	58	1215	280
1,3,5-Trimethylbenzene	APIRP45	1.62		Reg.			8	130	155/1	8.0	59		
		1.20		Azeo.	Me. Carb.	88	8	130	155/1	8.0	60		[m] 260
		[n] 0.83		do	do	80	8	130	155/1	8.0	61	2260	
		[n] 2.16											
MONOOLEFINS													
1-Pentene	Phillips	3.40	95.0	Reg.			4	200	160/1	4.5	62	1050	195
cis-2-Pentene	APIRP45	4.34		Azeo.	Methanol	90	4	200	180/1	4.0	63	408	82
trans-2-Pentene	do	2.10	99.90	Reg.			1	150	130/1	2.3	64	1425	367
2-Methyl-1-butene	General Motors	8.32		do			5	125	125/1	12.5	65		
		3.45	99.71	do			13	130	200/1	6.0	66	1405	450
3-Methyl-1-butene	Houdry Process	1.26	99.54	do			1	150	130/1	2.5	67	778	88
2-Methyl-2-butene	General Motors	15.0		do			6	125	125/1	12.5	68		
		8.46	99.81	do			8	130	155/1	8.0	69	2070	530
Cyclopentene	Atlantic	1.40		do			12	135	185/1	4.0	70	1030	240
	APIRP45	0.70											

[a] *(B)* following the name of a compound indicates that for the API–NBS series, it is a second (and usually slightly purer) sample of the given compound, the first sample of which is labeled *(A)*. (See reference [1]).

[b] The abbreviations represent the following laboratories: APIRP45; American Petroleum Institute Research Project 45 (formerly the American Petroleum Institute Hydrocarbon Research Project) at the Ohio State University, Columbus, Ohio. Penn State: Hydrocarbon Laboratory at the Pennsylvania State College, State College, Pa. General Motors: General Motors Corporation, Detroit, Mich. Ethyl: Ethyl Corporation, Detroit, Mich. NACA: National Advisory Committee for Aeronautics, Aeronautical Engine Research Laboratory, Cleveland, Ohio. Atlantic: Atlantic Refining Co., Philadelphia, Pa. Houdry Process: Houdry Process Corporation, Marcus Hook, Pa. Phillips: Phillips Petroleum Company, Bartlesville, Okla. Socony-Vacuum: Socony-Vacuum Laboratories, Paulsboro, N. J. APIRP6: American Petroleum Institute Research Project 6 at the National Bureau of Standards, Washington, D. C.

[c] The abbreviations are: Azeo., azeotropic; Reg., regular.

[d] The abbreviations are: Cell., Cellosolve (ethylene glycol monoethyl ether); Me. Cell., methyl Cellosolve (ethylene glycol monomethyl ether); Me. Carb., methyl Carbitol (diethylene glycol monomethyl ether).

[e] Approximate value obtained from the actual volume of hydrocarbon recovered by extracting the azeotrope-forming substance with water in separatory funnels.

[f] See reference [4] for further details.

[g] This is a second lot of 2-methylhexane supplied by the Ethyl Corporation.

[h] This is a second lot of 3-methylhexane supplied by the Ethyl Corporation.

[i] Calculated from the measured freezing points of three separate lots which were blended together for this charge.

[j] This charge consisted of fractions 154 to 213 from column 6 (see fig. 39).

[k] The total volume of the API–Standard sample was 1,550 ml.

[l] One of two similar charges.

[=] This charge consisted of material, having substantially the same composition, from each of the two previous distillations (see footnote 1).

[m] The distillation was begun with Cellosolve as the azeotrope-forming substance, but because of the small percentage of hydrocarbon in the azeotropic distillate, methyl Carbitol was added to complete the distillation.

[n] This is a second lot of 1-methyl-3-ethylbenzene supplied by the API Research Project 45.

[o] This material was given its final purification by B. J. Mair by the method of sulfonation and hydrolysis previously used to purify *m*-xylene. See reference [6].

[p] The 0.83 liter for this charge consisted of 0.39 liter (fractions 1 to 3, 57) from the first distillation in column 8 (see fig. 59), and 0.44 liter from the second distillation in column 8 (see fig. 60). The 2.16 liters is a second lot of 1,3,5-trimethylbenzene supplied by the API Research Project 45.

[q] Previously reported. See reference [1].

[r] The number of theoretical plates for this column was not determined.

[s] This starting material was obtained by distillation from a commercial "propylene" alkylate (propylene+isobutane).

[t] Obtained by purchase of commercially available material from the Connecticut Hard Rubber Company, New Haven, Conn.

[u] Obtained by purchase of commercially available material from the Dow Chemical Co., Midland, Mich.

[v] This charge consisted of 0.19 liter (fractions 130 to 134) from the distillation in column 14 (see fig. 16) and 1.61 liters from the distillation in column 4 (see fig. 17).

pentane, 3-methyl-3-ethylpentane, 2,3,4-trimethylpentane, 1-methyl-2-ethylbenzene, 1-methyl-3-ethylbenzene, 1,2,3-trimethylbenzene (*B*), 1,3,5-trimethylbenzene, *cis*-2-pentene, *trans*-2-pentene, and cyclopentene (one-third).

By the Hydrocarbon Laboratory at the Pennsylvania State College, State College, Pa., under the supervision of F. C. Whitmore: 2,4-Dimethylhexane, 2,5-dimethylhexane, and 2,3,3-trimethylpentane.

By the General Motors Corporation Research Laboratories, Detroit, Mich., through T. A. Boyd and W. G. Lovell: 2,3-Dimethylpentane, 2-methyl-1-butene, 2,2,3-trimethylpentane, 2-methyl-2-butene.

By the Ethyl Corporation, Detroit, Mich., through George Calingaert: 2-Methylhexane, 3-methylhexane, and 3,3-dimethylpentane.

By the National Advisory Committee for Aeronautics, through its Aeronautical Engine Research Laboratory at Cleveland, Ohio: 1-Methyl-4-ethyl- benzene, 1,2,4-trimethylbenzene (*B*).

By the Atlantic Refining Co., Philadelphia, P through T. G. Delbridge: Cyclopentene (tw thirds).

By the Houdry Process Corporation, Marc Hook, Pa., through E. A. Smith: 3-Methyl- butene.

By the Phillips Petroleum Co., Bartlesvill Okla., through F. E. Frey: 1-Pentene.

By the Socony-Vacuum Laboratories, Paul boro, N. J., through L. C. Beard, Jr.: 2,2-D methylpentane.

By the API Research Project 6 at the Nation Bureau of Standards, under the supervision F. D. Rossini: 2,4-Dimethylpentane, *n*-octan and *n*-propylbenzene (B).

Table 1 summarizes the amounts of the starti materials, and gives some additional informati as to the source and purity.

III. Purification

The procedure followed in the process of purification and determination of purity can be illustrated by considering a given compound, as follows:

The starting material for 2-methyl-1-butene was 8.3 liters of hydrocarbon, supplied by the Research Laboratories of the General Motors Corporation and estimated by them to be about 90 per cent pure. The 8.3 liters of starting material was put into column 5 (having approximately 125 theoretical plates at total reflux) on December 8, 1944, and the distillation, running 24 hours a day, 7 days a week, at a reflux ratio of 125/1 and with a rate of collection of distillate of 12.5 ml/hr, was concluded on January 12, 1945. The distillation time was 840 hours, with about 30 hours to reach equilibrium at the start. The details of the assembly, testing, and operation of the distilling columns used in this work are given in reference [4]. The records from the distillation yielded accurate values of the boiling point, to the nearest 0.01° C at the given controlled pressure of 724.5 mm Hg, of the distillate as a function of its volume [4]. The refractive index, n_D at 25° C, of each of the fractions of distillate was measured to ±0.0001, using NBS Standard Samples of 2,2,4-trimethylpentane, methylcyclohexane, and toluene as reference substances, on Valentine refractom eters, Abbe-type, graduated directly to 0.000 The purity of four selected fractions was dete mined by measuring freezing points, using th apparatus and procedure already described [5 From the freezing points of these four fraction the upper curve of figure 65 was constructed giving the freezing point of the distillate and it purity (scale at upper right) as a function of it volume over the range of higher purity. Figur 65 also shows the refractive index (n_D at 25° C and the boiling point (in ° C at 724.5 mm Hg of the distillate as a function of its volume. Fig ure 1 gives a view of the freezing-point apparatu in operation. A typical time-temperature melt curve is shown in figure 2.

From the first distillation, it is seen that 3.4 liters of material of 99.7 mole percent purity marked X in figure 65, was available for the second distillation. This material was put into Column 13 (having approximately 130 theoretical plate at total reflux) on February 7, 1945, and the dis tillation, running 24 hours a day, 7 days a week at a reflux ratio of 200/1 and with a rate of collec tion of distillate of 6.0 ml/hr, was concluded o March 5, 1945. The distillation time was 62 hours, with about 30 hours to reach equilibrium

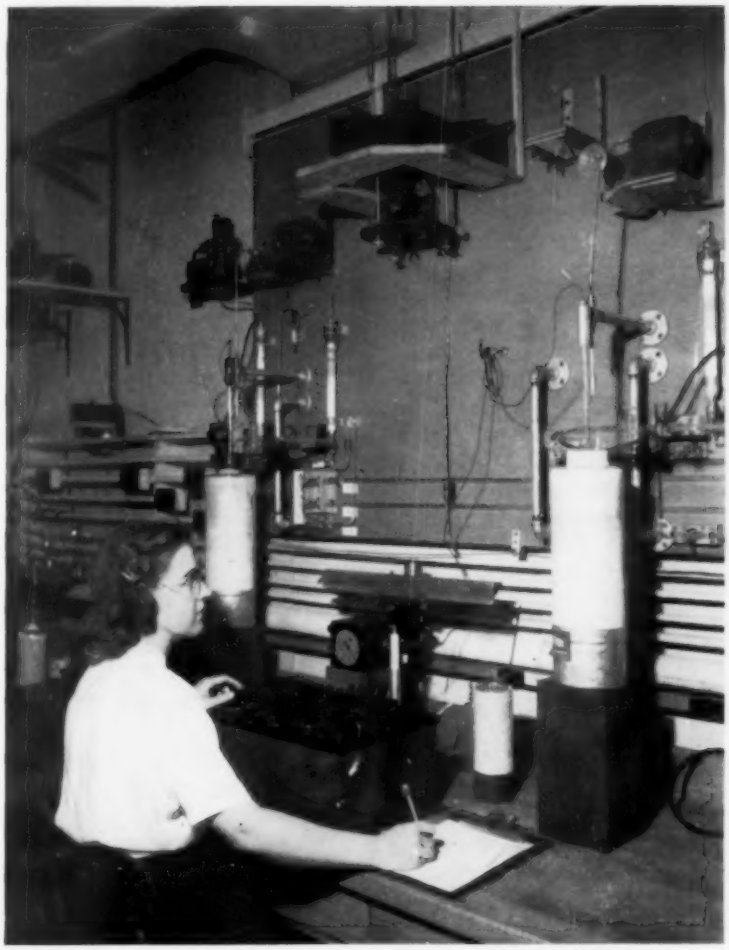

FIGURE 1.—*Freezing-point apparatus for determining the purity of hydrocarbons.*

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t the start. As before, measurements and plots were made of refractive index, boiling point, freezing point, and purity, with the results shown in figure 66. The part marked Z was taken as the API–NBS sample and the parts marked Y were taken as the material for the standard sample. The material marked W in figures 65 and 66 was returned to the supplier. The final products for this compound consisted of an API–NBS sample having a volume of 0.45 liter and a purity of 99.89 ±0.08 mole percent and an API-Standard sample having a volume of 1.41 liters and a purity of 99.86 ±0.08 mole percent.

In addition to the name of the laboratory supplying the starting materials, table 1 and its footnotes, give complete information for each distillation for each of the compounds.

Figures 3 to 70, inclusive, show graphically the results of the distillations listed in table 1. These figures give, as a function of the volume of hydrocarbon distillate, the refractive index (n_D at 25° C to ±0.0001 deg C), the boiling point of the distillate (at the controlled pressure of 724.5 mm Hg, to ±0.01 deg C), the freezing point of selected fractions of hydrocarbon distillate (in air at 1 atm, usually with a precision near ±0.003 deg C), and the purity of the hydrocarbon distillate. W, X, Y, and Z indicate the disposition of the material, as follows: W, returned to the laboratory supplying the material; X, blended for redistillation; Y, used for the API-Standard material; Z, used for the API-NBS material.

In connection with the purification of hydrocarbons, the following points are to be noted: (a) A logical, simple purification following the original synthesis or other preparation of a given hydrocarbon concentrate will usually remove all impurities except more-or-less close-boiling isomers, (b) an impurity of several percent of close-boiling isomers will have relatively little effect on the boiling point, refractive index, or density, but will normally affect the freezing point appreciably, (c) in a series of fractions obtained from a distillation at high efficiency of a hydrocarbon containing close-boiling isomers as impurity, the fractions of highest purity will be beyond or ahead of the middle portion of the distillate as frequently as in the middle portion, (d) for producing material of highest purity, the blending of the fractions of distillate can be done safely only on the basis of the freezing points of selected fractions. An example of a case where the purest material is near the beginning of a distillation is shown in figure 25, for 2,2-dimethylhexane, and an example of a case where the purest material is at the very end of the distillation is shown in figure 63, for *cis*-2-pentene.

IV. Freezing Points, Cryoscopic Constants, and Purity

Table 2 gives the following information for each of the compounds (except as otherwise indicated): The kind of time-temperature curves; whether freezing or melting, used to determine the freezing point [5]; the freezing point of the actual sample, in air at 1 atm [5], for both the API-Standard and the API-NBS lots; the calculated value of the freezing point for zero impurity [5]; the value of the cryoscopic constant determined from the lowering of the freezing point on the addition of a known amount of an appropriate impurity [5]; and the resulting calculated amount of impurity in the API-Standard and the API-NBS material.

Grateful acknowledgment is made to the organizations and individuals listed in section II of this report for their contributions of materials for use in this work.

TABLE 2.—*Freezing points and purity of 37 API-Standard and API-NBS hydrocarbons*

Compound [a]	Kind of time temperature observations used to determine the freezing point [b]	Freezing point of the actual selected sample, in air at 1 atm [c]		Freezing point for zero impurity in air at 1 atm [c]	Cryoscopic constant [b] A	Calculated amount of impurity in the actual selected sample [d]	
		API-Standard	API-NBS			API-Standard	API-NBS
				PARAFFINS			
		°C	°C	°C	deg.-1	Mole %	Mole %
2-Methylhexane	M	−118.321	−118.311	−118.270±0.015	[e] (0.0445)	0.23±0.07	0.18±0.07
3-Methylhexane						[f] (.25±0.15)	[f] (.20±0.15)
3-Ethylpentane	M	−118.620	−118.605	−118.593±0.010	[e] (.0476)	.13±0.03	.06±0.03
2,2-Dimethylpentane	F and M	−123.858	−123.852	−123.790±0.020	[e] (.0316)	.21±0.06	.19±0.06
2,3-Dimethylpentane						[f] (.25±0.15)	[f] (.20±0.15)
2,4-Dimethylpentane	F and M	−119.280	−119.263	−119.230±0.015	[e] (.0340)	.17±0.05	.12±0.05
3,3-Dimethylpentane	M	−134.51(I)	−134.51(I)	−134.46 ±0.04(I)	[e] (.0442) (I)	.22±0.18	.22±0.18
				−134.95 ±0.05(II)(u)			
				−135.36 ±0.05(III)(u)			
n-Octane	F	−56.810	−56.807	−56.798±0.006	[e] (.0530)	.06±0.04	.05±0.04
2-Methylheptane	M	−109.129	−109.114	−109.04 ±0.04	.0458	.41±0.18	.34±0.18
3-Methylheptane	M	−120.585	−120.565	−120.50 ±0.04	.0587	.50±0.23	.38±0.23
4-Methylheptane	M	−120.977	−120.975	−120.955±0.012	.0563	.12±0.07	.11±0.07
3-Ethylhexane						[f] (.30±0.20)	[f] (.25±0.20)
2,3-Dimethylhexane	M	−121.261	−121.246	−121.18 ±0.08	.0354	.29±0.11	.23±0.11
2,3-Dimethylhexane						[f] (.30±0.20)	[f] (.25±0.20)
2,4-Dimethylhexane						[f] (.30±0.20)	[f] (.25±0.20)
2,5-Dimethylhexane	F and M	−91.265	−91.258	−91.200±0.015	.0467	.30±0.09	.27±0.09
3,3-Dimethylhexane	M	[g] −126.18	[g] −126.16	[g](−126.10 ±0.05)	[e] (.04)	.30±0.20	.25±0.20
3,4-Dimethylhexane						[f] (.30±0.20)	[f] (.25±0.20)
2-Methyl-3-ethylpentane	M	−115.002	−115.001	−114.960±0.020	.0344	.23±0.11	.22±0.11
3-Methyl-3-ethylpentane	F and M	−90.890	−90.888	−90.870±0.010	.0392	.08±0.04	.07±0.04
2,2,3-Trimethylpentane	M	−112.375	−112.350	−112.27 ±0.05	.0401	.42±0.20	.32±0.20
2,2,3-Trimethylpentane	F	−101.341	−101.034	−100.70 ±0.10	.0062	.46±0.08	.21±0.08
2,3,4-Trimethylpentane	M	−109.257	−109.252	−109.210±0.015	[e] (.04122)	.19±0.06	.17±0.06
				ALKYLBENZENES			
n-Propylbenzene (*B*)	M	−99.574(I)	−99.560(I)	−99.500±0.024(I)	[h] 0.034(I)	0.25 ±0.08	0.20±0.08
	M			−101.55 ±0.03(II)(u)	.032(II)		
1-Methyl-2-ethylbenzene	M	−80.917(I)	−80.909(I)	−80.833±0.020(I)	.0346(I)	.27 ±0.07	.24±0.07
	M			−86.556±0.020(II)(u)	[h] .033(II)		
1-Methyl-3-ethylbenzene	M	−95.66(I)	−95.63(I)	−95.55 ±0.05(I)	.029(I)	.32 ±0.15	.23±0.15
	M			−96.96 ±0.05(II)(u)	[h] .029(II)		
1-Methyl-4-ethylbenzene	M	−62.400	−62.367	−62.350±0.010	.0344	.17 ±0.03	.06±0.03
1,2,3-Trimethylbenzene(*B*)	M	−25.386	−25.381	−25.375±0.006	.0164	.018±0.012	.010±0.009
1,2,4-Trimethylbenzene(*B*)	M	−43.912(I)	−43.907(I)	−43.80 ±0.07(I)	.0282(I)	.32 ±0.20	.30±0.20
				−49.00 ±0.07(II)(u)			
1,3,5-Trimethylbenzene	M	−44.741(I)		−44.720±0.010(I)	[e] (.022) (I)	.05 ±0.02	
				−49.790±0.020(II)(u)			
				−51.680±0.020(III)(u)			
				MONOOLEFINS			
1-Pentene	M	−165.40	−165.37	−165.27 ±0.08	0.051	0.66 ±0.40	0.51 ±0.40
cis-2-Pentene	M	−151.443	−151.403	−151.370±0.025	.062	.45 ±0.15	.20 ±0.15
trans-2-Pentene	F and M	−140.252	−140.248	−140.235±0.010	.0530	.09 ±0.05	.07 ±0.05
2-Methyl-1-butene	F and M	−137.587	−137.582	−137.560±0.015	.0516	.14 ±0.08	.11 ±0.08
3-Methyl-1-butene	F and M	−168.541	−168.538	−168.500±0.020	.0580	.24 ±0.12	.22 ±0.12
2-Methyl-2-butene	F and M	−133.793	−133.792	−133.780±0.010	[e] (.0462)	.06 ±0.05	.055±0.046
Cyclopentene	F and M	−135.086	−135.082	−135.070±0.010	.0212	.034±0.021	.025±0.021

[a] A letter (*B*) following the name of a compound indicates that, for the API-NBS series, it is a second (and usually slightly purer) sample of the given compound, the first sample of which is labeled (*A*). (See reference [1].)

[b] *F* indicates freezing and *M* indicates melting. See reference [5] for experimental details and the definition of the cryoscopic constant.

[c] When a given hydrocarbon has more than one crystalline form, the several forms will be labeled I, II, and III, in order of decreasing temperature of fusion (or freezing point). Forms other than I will be, at their respective freezing points, in metastable equilibrium with the under-cooled liquid, but will be unstable with respect to transition to some other solid form at the same temperature and pressure (one atmosphere). This is indicated by a letter *u* in parentheses following the Roman numeral.

[d] The values in this column, except as otherwise indicated, were calculated as described in reference [5], using the values of the cryoscopic constants and freezing points for zero impurity given in the preceding columns.

[e] Not determined in this investigation. From the "*x*" tables of the American Petroleum Institute Research Project 44 [7].

[f] Estimated by analogy with isomers subjected to similar purification.

[g] The uncertainty in this value may be several hundredths of a degree.

[h] Estimated from the measured value of the cryoscopic constant.

V. References

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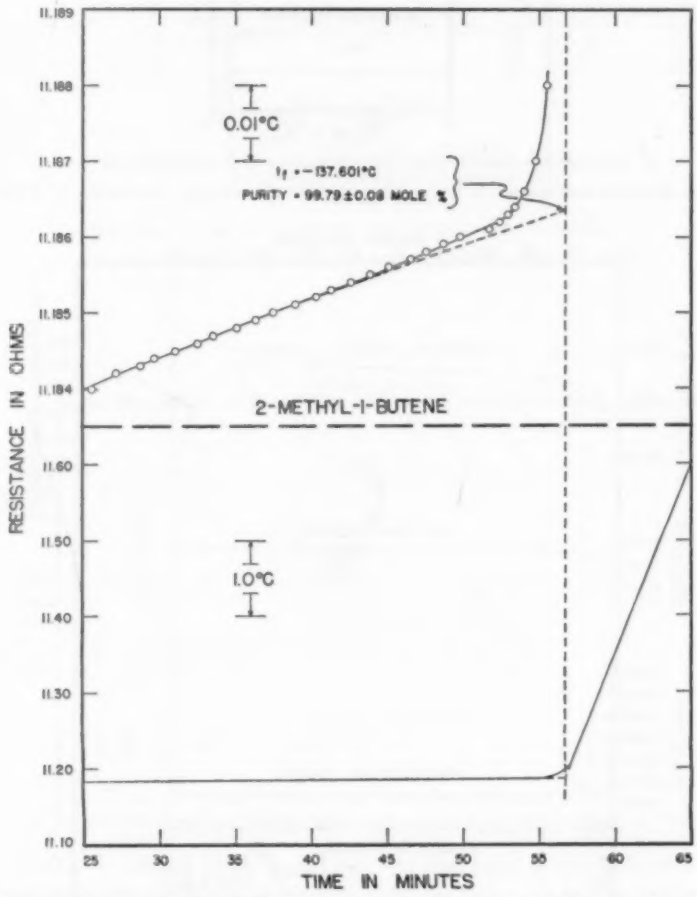

FIGURE 2.— *Time-temperature warming curves for determining the freezing point of a sample of 2-methyl-1-butene.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer (0.1 ohm is approximately 1.0° C). The scale of abscissas gives the time in minutes. The same data are used for both curves, but the scale of temperature (or resistance) for the upper curve is magnified one hundred times that for the lower curve.

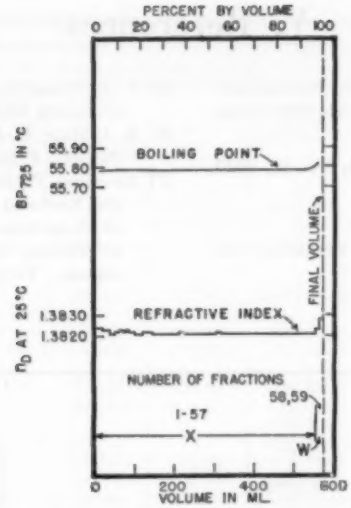

FIGURE 3.—*Results of the first distillation of 2-methylhexane.*

Azeotropic distillation with methanol at 725 mm Hg in still 11 (4/18/44 to 5/10/44). See footnote "g" of table 1

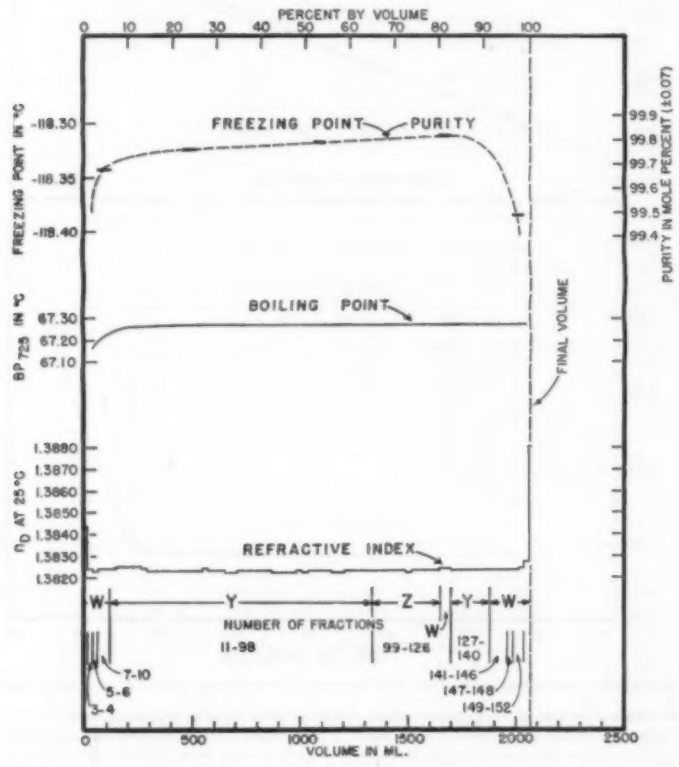

FIGURE 4.—*Results of the second and final distillation of 2-methylhexane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 10 (10/11/44 to 11/9/44). 50 ml of fractions 99 to 126 (marked "W") was returned to the supplier as a "best" sample.

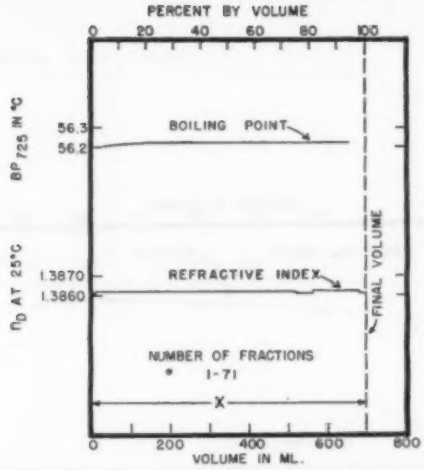

FIGURE 5.—*Results of the first distillation of 3-methylhexane.*

Azeotropic distillation with methanol at 725 mm Hg in still 11 (5/10/44 to 6/3/44).

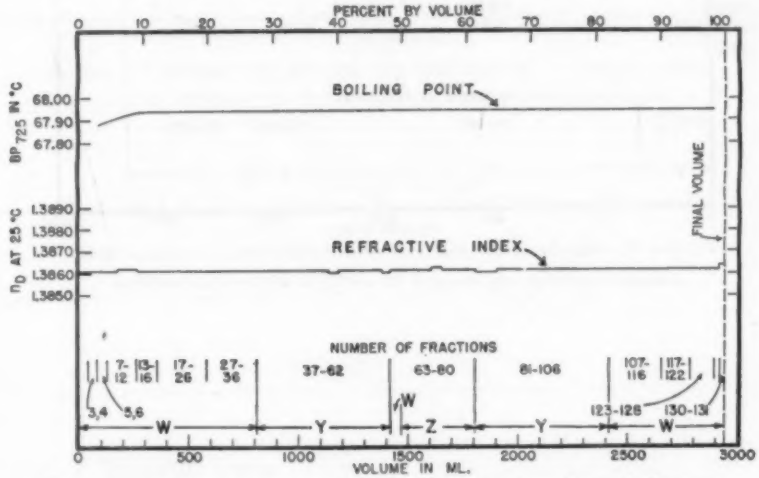

FIGURE 6.—*Results of the second and final distillation of 3-methylhexane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 7 (10/17/44 to 11/11/44). See footnote "h" of table 1. 50 ml of fractions 63 to 80 (marked "W") was returned to the supplier as a "best" sample.

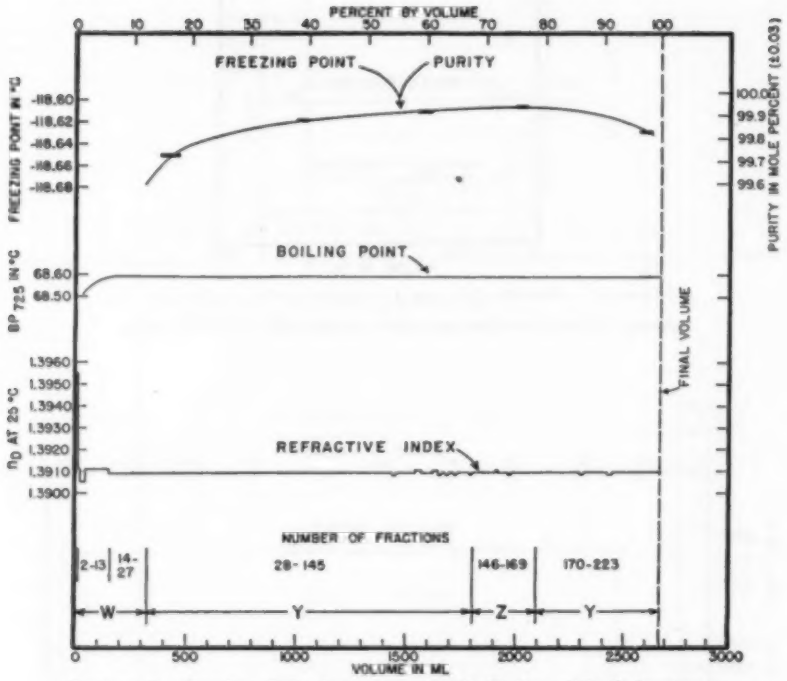

FIGURE 7.—*Results of the first and only distillation of 3-ethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 10 (8/22/44 to 10/4/44).

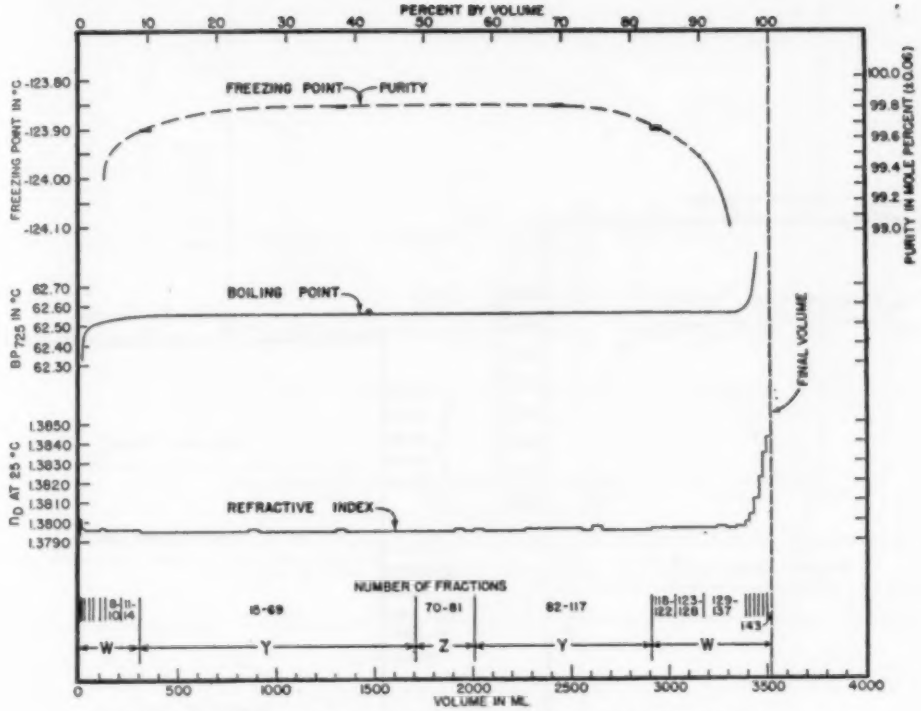

FIGURE 8.—*Results of the first and only distillation of 2,2-dimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 7 (7/31/44 to 8/28/44).

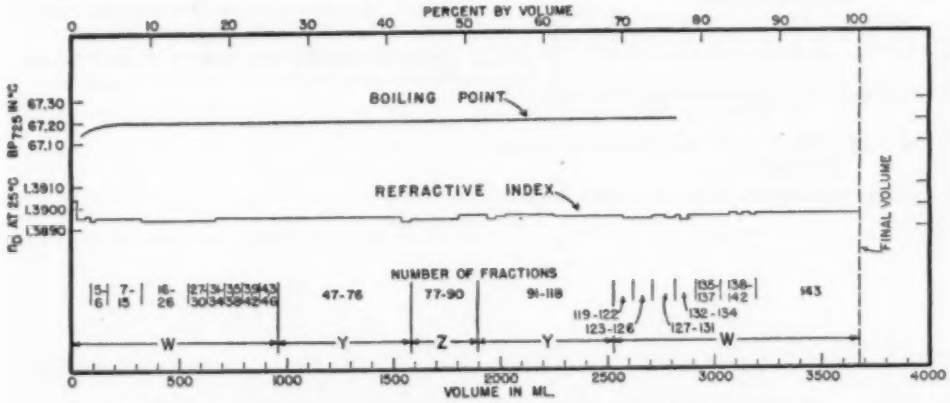

FIGURE 9.—*Results of the first and only distillation of 2,3-dimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 8 (8/16/44 to 9/11/44).

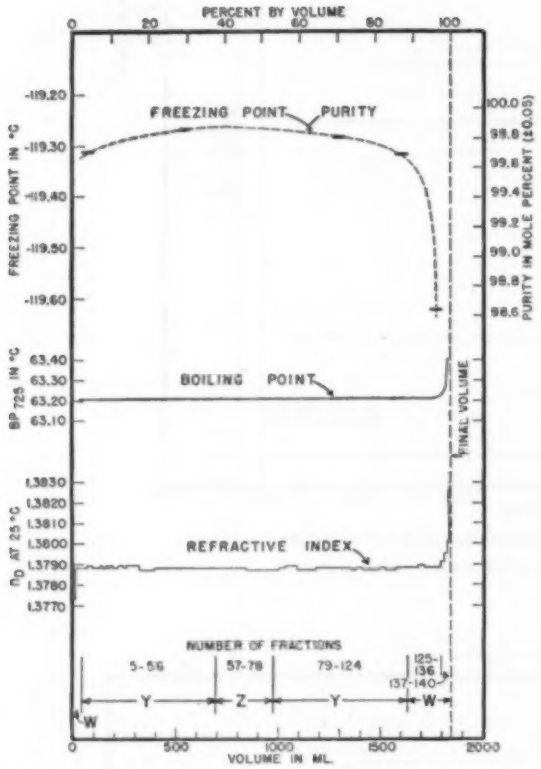

FIGURE 10.—*Results of the first and only distillation of 2,4-dimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 4 (8/14/44 to 9/11/44).

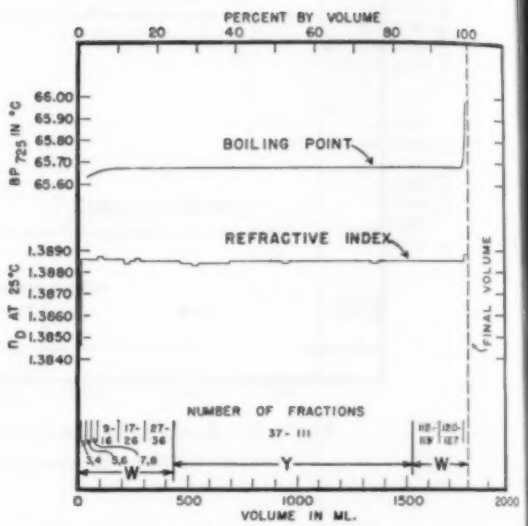

FIGURE 11.—*Results of the first and only distillation of the first lot of 3,3-dimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 9 (11/2/44 to 11/27/44).

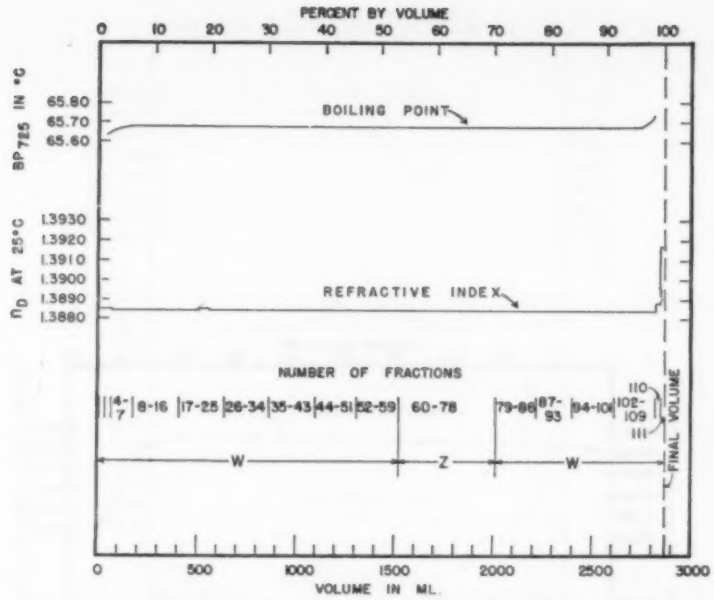

FIGURE 12.—*Results of the first and only distillation of the second lot of 3,3-dimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 7 (1/22/45 to 2/17/45).

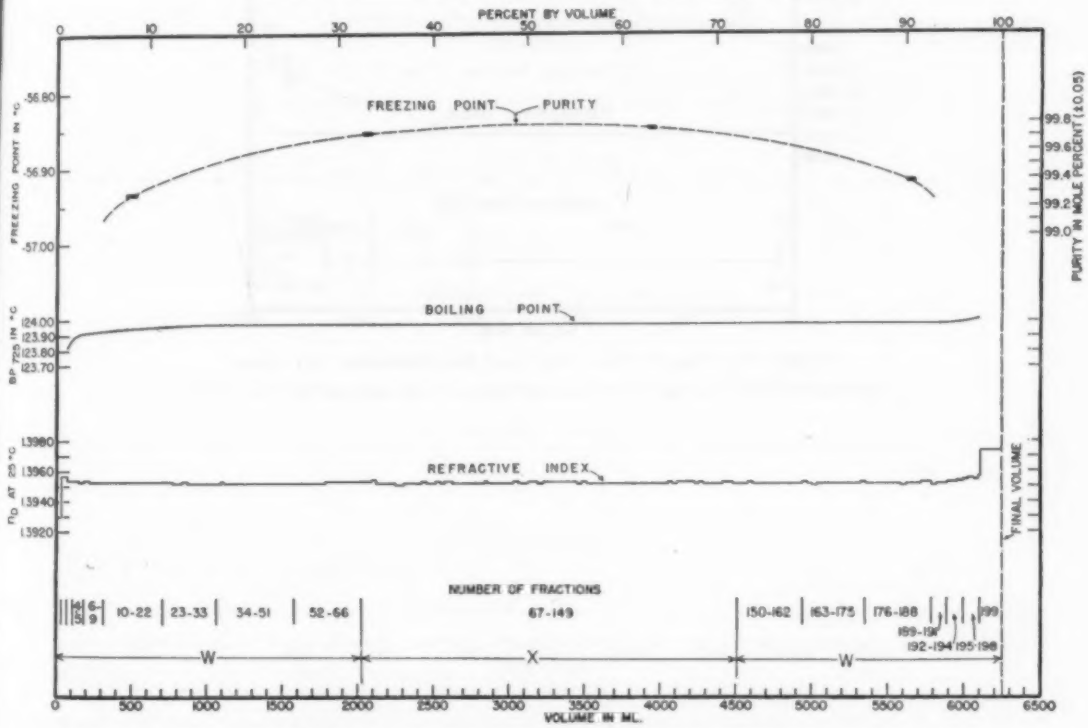

FIGURE 13.—*Results of the first distillation of n-octane.*

Regular distillation at 725 mm Hg in still 13 (4/6/45 to 5/14/45).

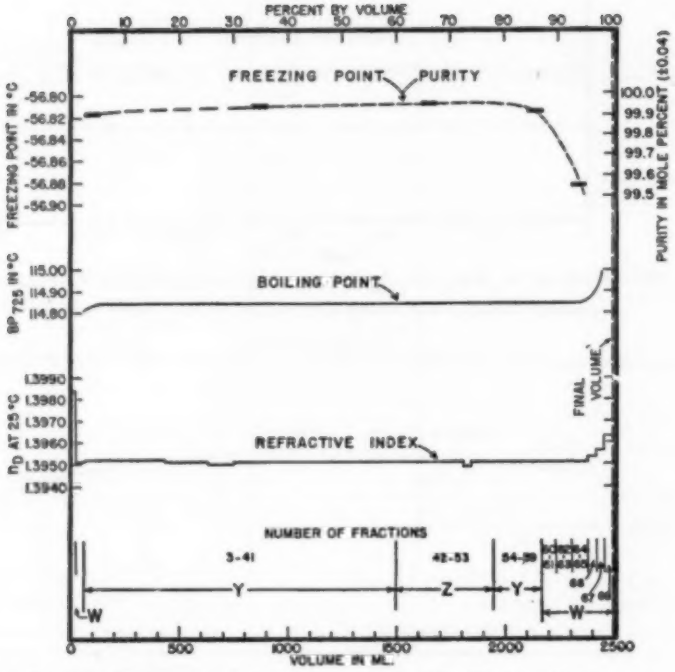

FIGURE 14.—*Results of the second and final distillation of n-octane.*

Azeotropic distillation with ethylene glycol monethyl ether at 725 mm Hg in still 15 (5/26/45 to 6/8/45).

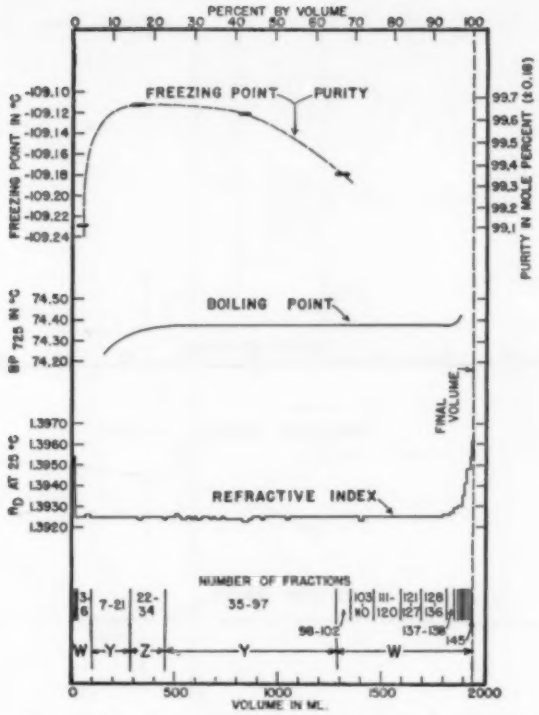

FIGURE 15.—*Results of the first and only distillation of 2-methylheptane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 7 (4/24/45 to 5/20/45).

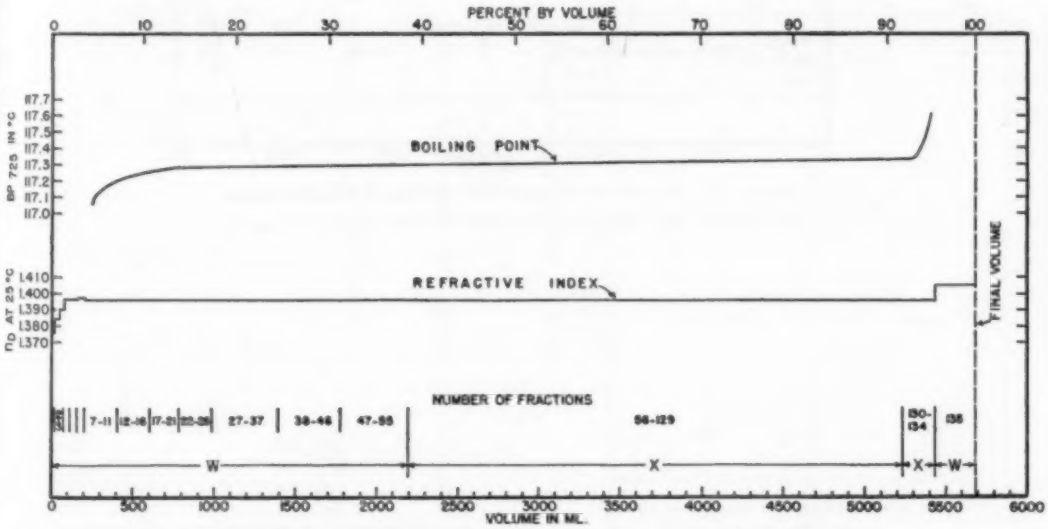

FIGURE 16.—*Results of the first distillation of 3-methylheptane.*

Regular distillation at 725 mm Hg in still 14 (8/30/44 to 9/20/44). Fractions 56 to 129 were used for the charge in the following distillation (see fig. 17), and fractions 130 to 134 were used for the azeotropic distillation in still 8 (see fig. 18 and footnote "w" of table 1).

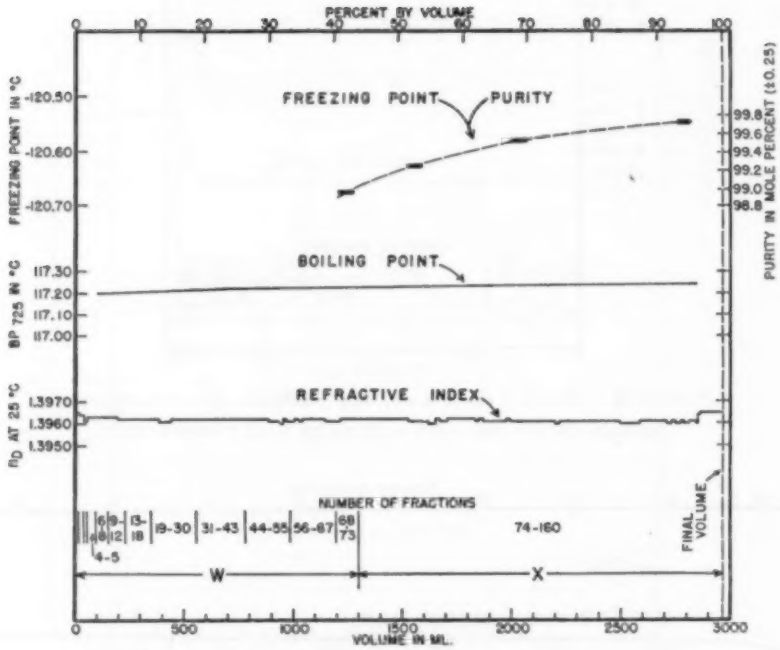

FIGURE 17.—*Results of the second distillation of 3-methylheptane.*

Regular distillation at 725 mm Hg in still 4 (3/3/45 to 4/1/45). See legend of figure 16.

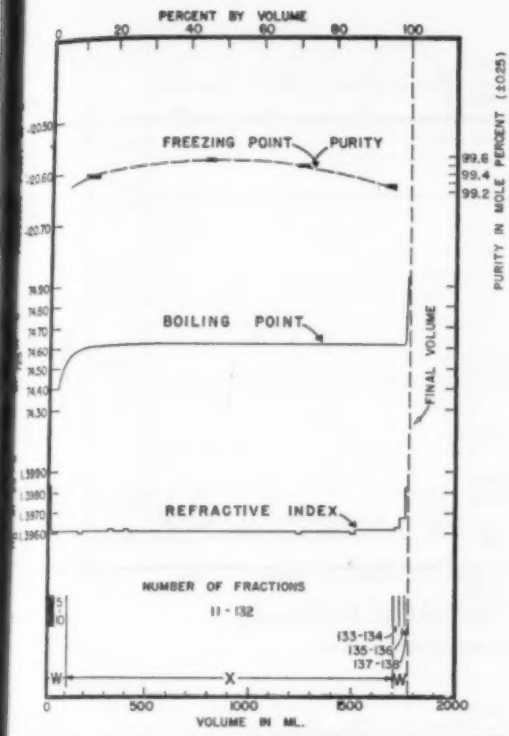

FIGURE 18.—*Results of the third distillation of 3-methylheptane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 8 (5/7/45 to 5/31/45). See footnote "w" of table 1.

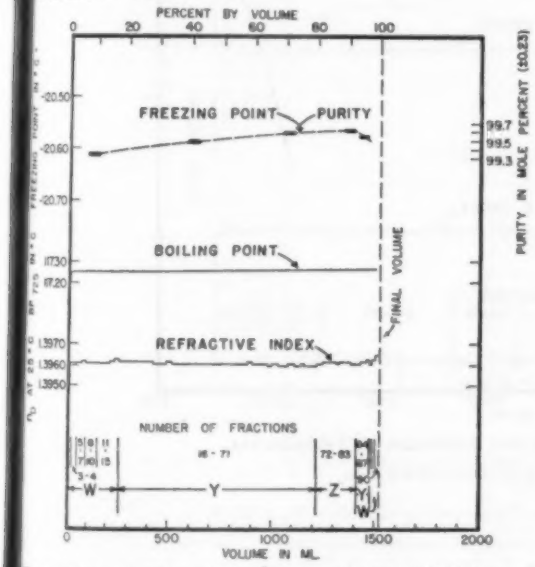

FIGURE 19.—*Results of the fourth and final distillation of 3-methylheptane.*

Regular distillation at 725 mm Hg in still 4 (6/12/45 to 6/30/45).

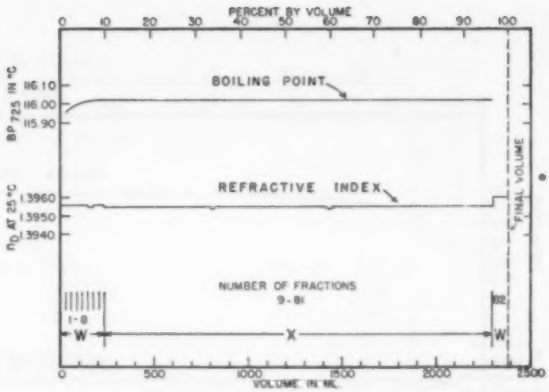

FIGURE 20.—*Results of the first distillation of 4-methylheptane.*

Regular distillation at 725 mm Hg in still 12 (1/25/45 to 2/18/45).

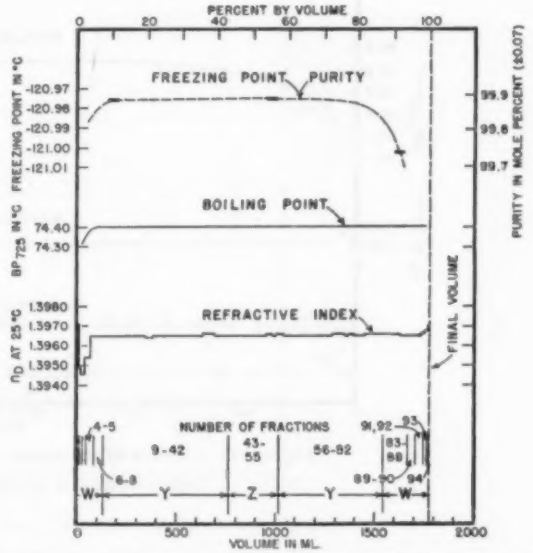

FIGURE 21.—*Results of the second and final distillation of 4-methylheptane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 14 (3/29/45 to 4/23/45).

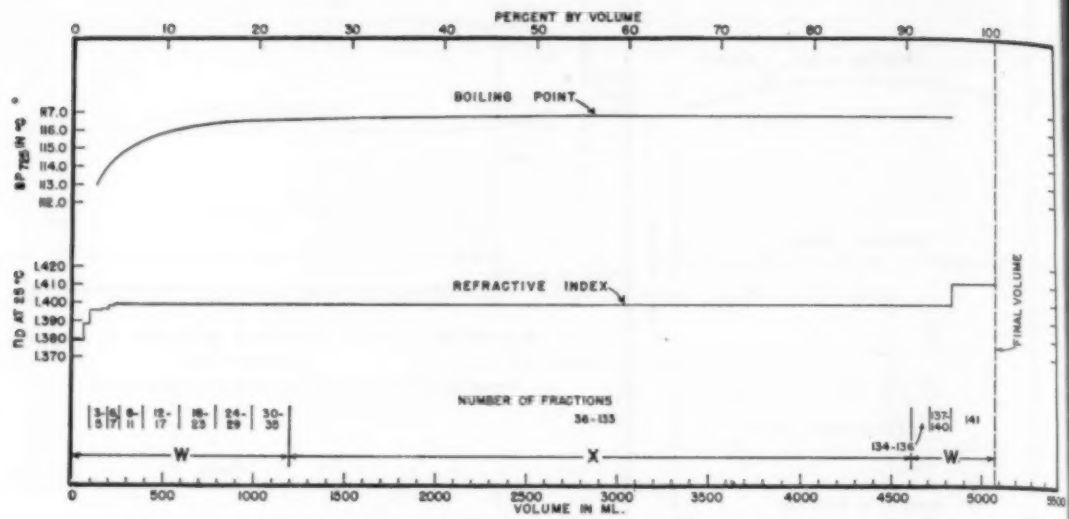

FIGURE 22.—*Results of the first distillation of 3-ethylhexane.*

Regular distillation at 725 mm Hg in still 7 (9/19/44 to 10/6/44).

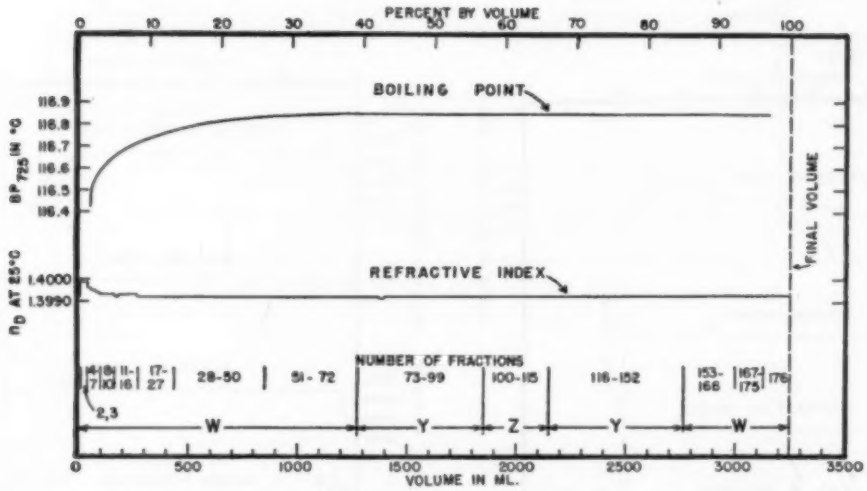

FIGURE 23.—*Results of the second and final distillation of 3-ethylhexane.*

Regular distillation at 725 mm Hg in still 10 (3/21/45 to 4/23/45).

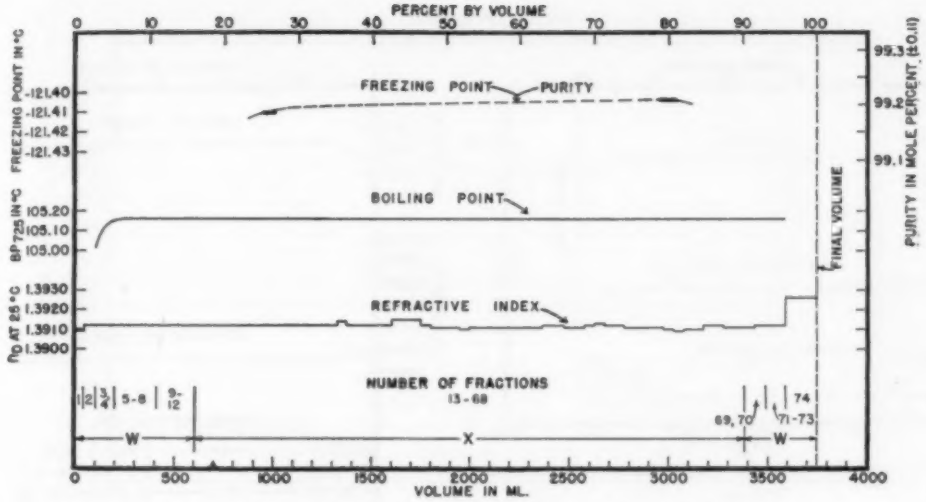

FIGURE 24.—*Results of the first distillation of 2,2-dimethylhexane.*

Regular distillation at 725 mm Hg in still 15 (11/30/44 to 12/15/44).

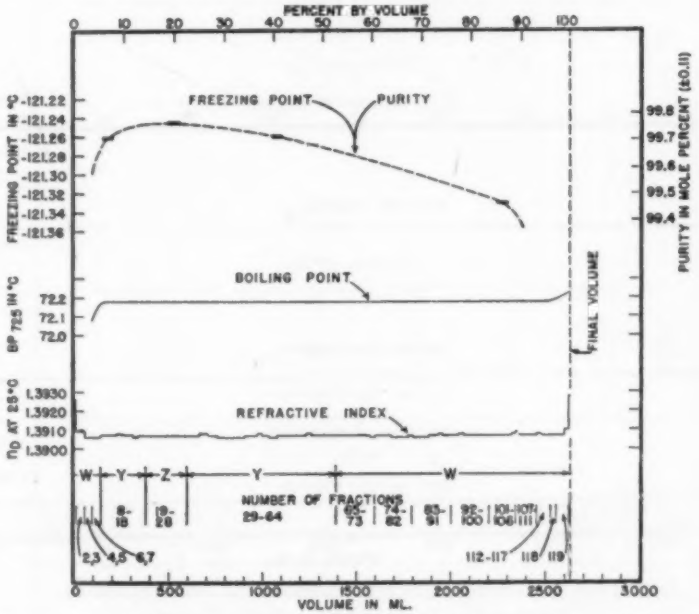

FIGURE 25.—*Results of the second and final distillation of 2,2-dimethylhexane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 13 (1/9/45 to 2/7/45).

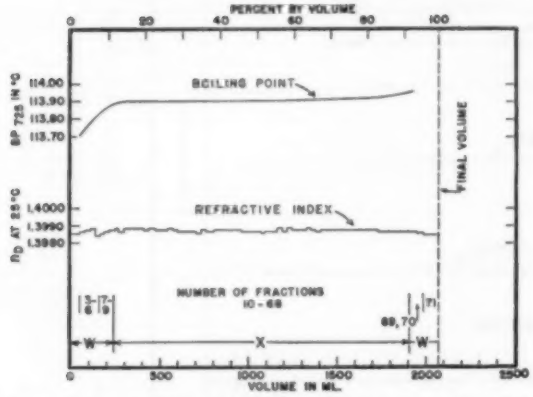

FIGURE 26.—*Results of the first distillation of 2,3-dimethylhexane.*

Regular distillation at 725 mm Hg in still 12 (12/9/44 to 1/2/45).

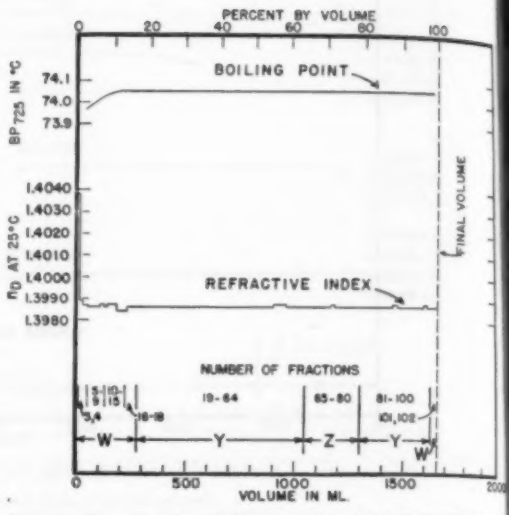

FIGURE 27.—*Results of the second and final distillation of 2,3-dimethylhexane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 8 (2/5/45 to 2/28/45).

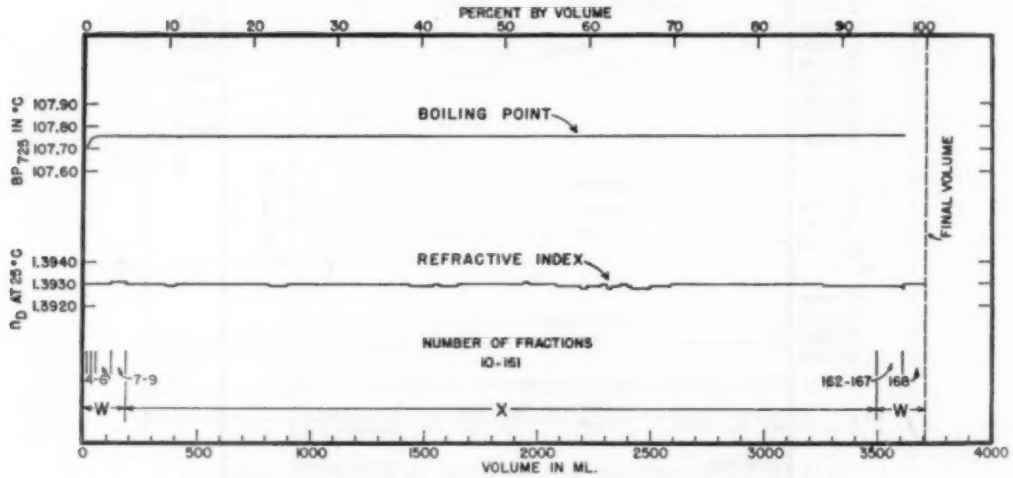

FIGURE 28.—*Results of the first distillation of 2,4-dimethylhexane.*

Regular distillation at 725 mm Hg in still 9 (7/31/44 to 8/30/44).

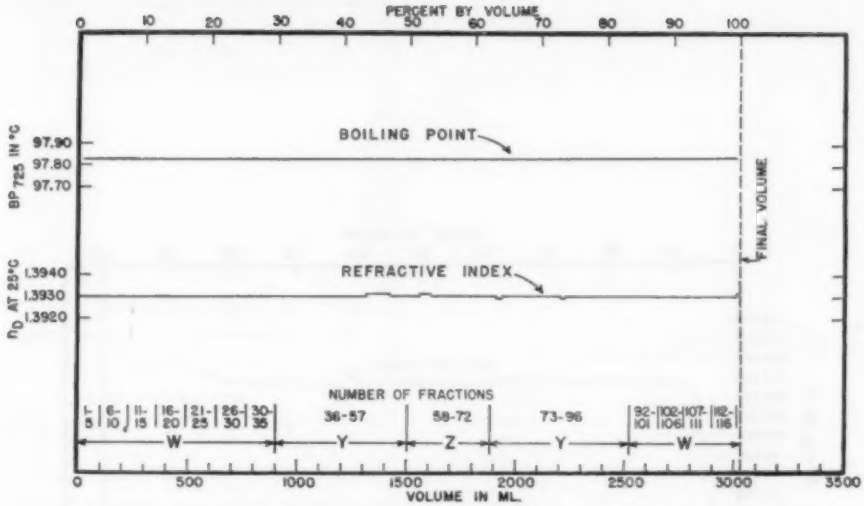

FIGURE 29.—*Results of the second and final distillation of 2,4-dimethylhexane.*

Azeotropic distillation with ethylene glycol monomethyl ether at 725 mm Hg in still 7 (11/11/44 to 12/8/44).

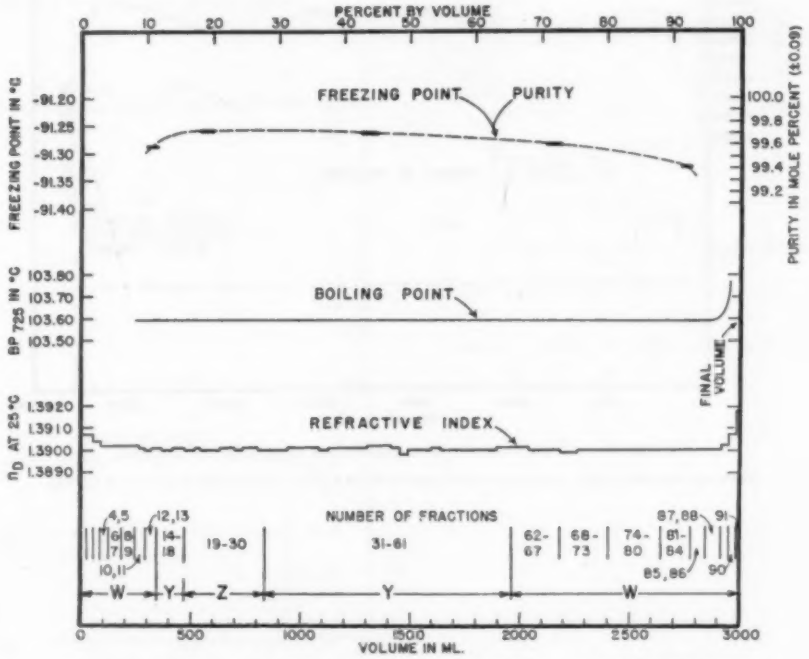

FIGURE 30.—*Results of the first and only distillation of 2,5-dimethylhexane.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 14 (10/23/44 to 11/12/44).

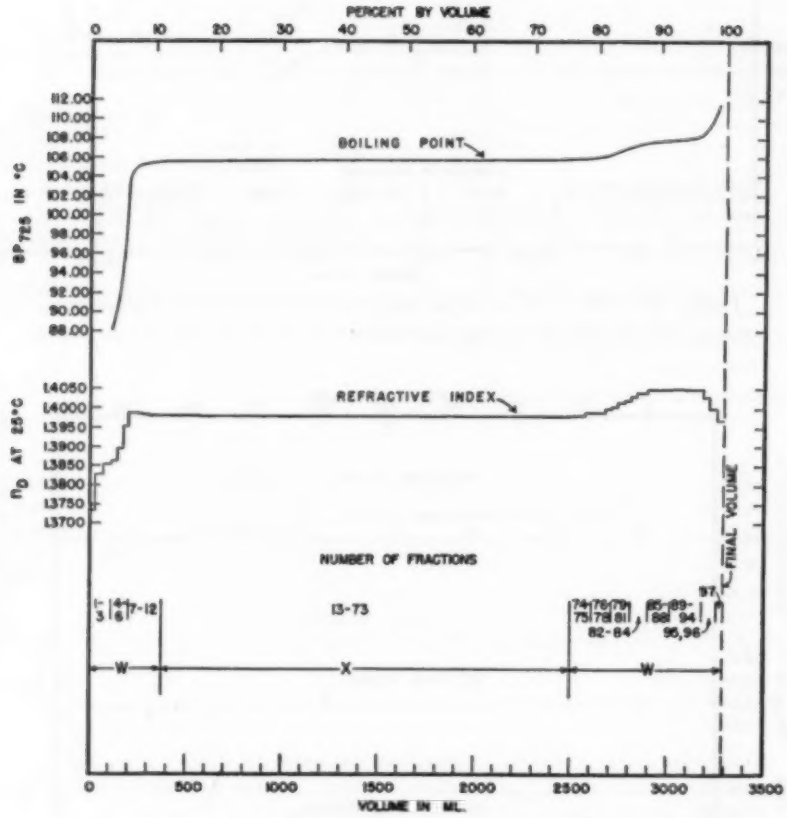

FIGURE 31.—*Results of the first distillation of 3,3-dimethylhexane.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 14 (9/21/44 to 10/7/44).

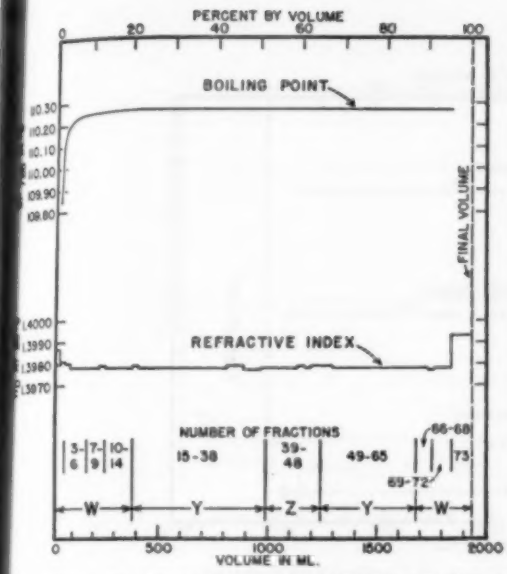

FIGURE 32.—*Results of the second and final distillation of 3,3-dimethylhexane.*

Regular distillation at 725 mm Hg in still 12 (1/3/45 to 1/23/45).

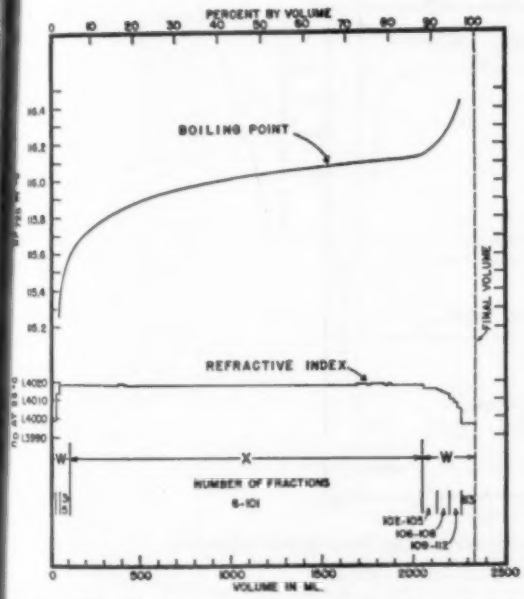

FIGURE 33.—*Results of the first distillation of 3,4-dimethylhexane.*

Regular distillation at 725 mm Hg in still 12 (11/16/44 to 12/8/44).

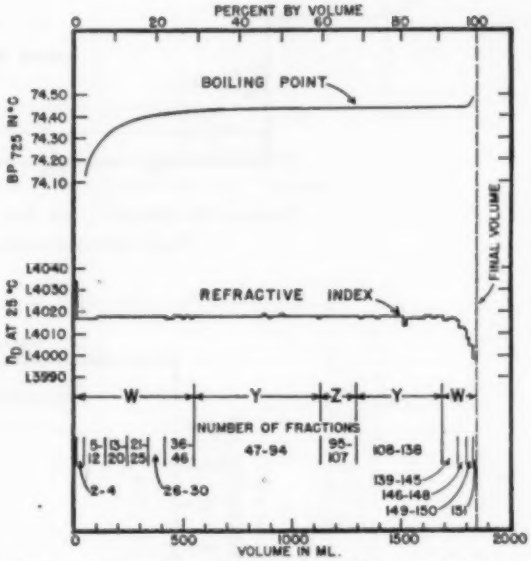

FIGURE 34.—*Results of the second and final distillation of 3,4-dimethylhexane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 8 (4/6/45 to 5/5/45).

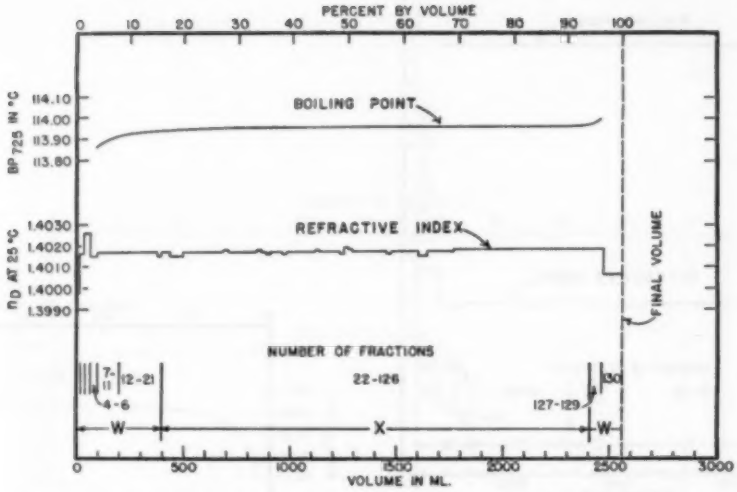

FIGURE 35.—*Results of the first distillation of 2-methyl-3-ethylpentane*

Regular distillation at 725 mm Hg in still 12 (8/30/44 to 9/26/44).

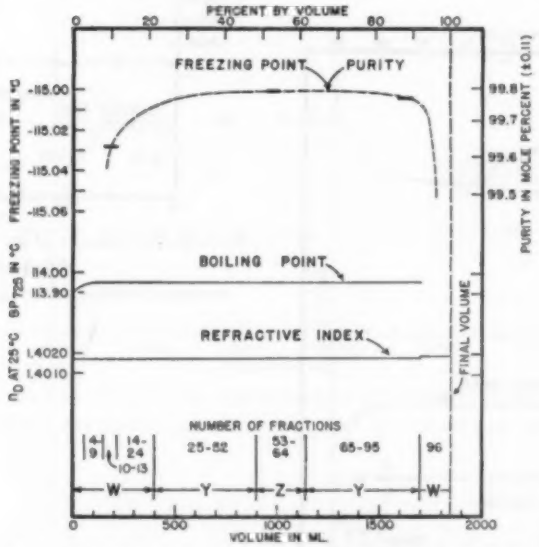

FIGURE 36.—*Results of the second and final distillation of 2-methyl-3-ethylpentane.*

Regular distillation at 725 mm Hg in still 4 (4/3/45 to 4/20/45).

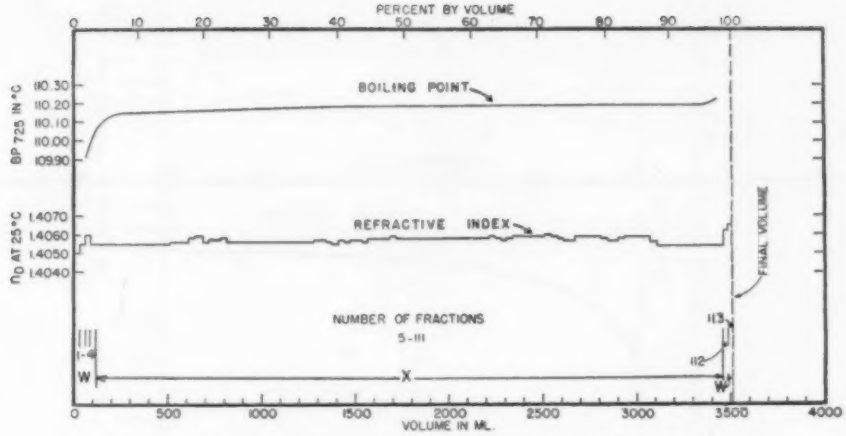

FIGURE 37.—*Results of the first distillation of 3-methyl-3-ethylpentane.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 14 (10/7/44 to 10/23/44).

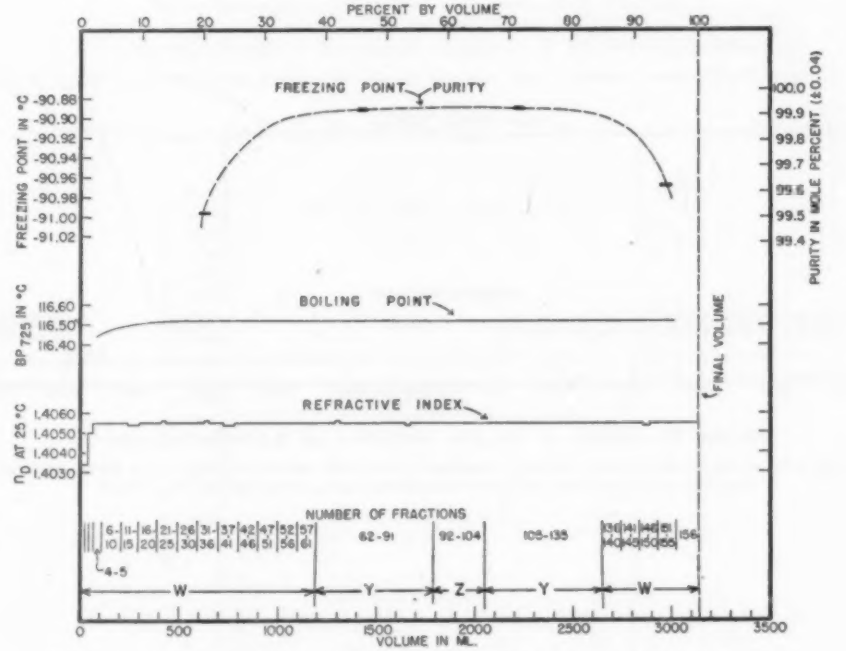

FIGURE 38.—*Results of the second and final distillation of 3-methyl-3-ethylpentane.*

Regular distillation at 725 mm Hg in still 9 (3/1/45 to 3/29/45).

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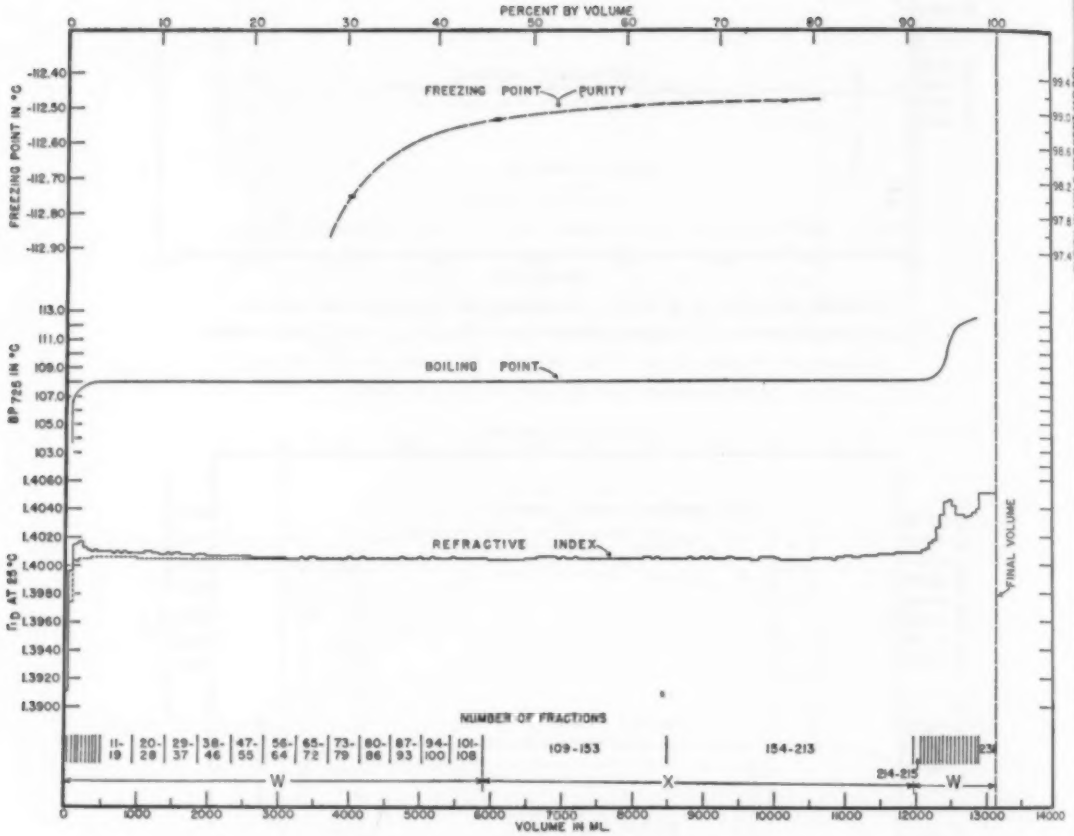

FIGURE 39.—*Results of the first distillation of 2,2,3-trimethylpentane.*

Regular distillation at 725 mm Hg in still 6 (9/12/44 to 10/23/44). Fractions 109 to 153 were used for the charge for the second distillation (see fig. 40). Fractions 154 to 213 were used for the fourth distillation (see fig. 42 and footnote "j" of table 1).

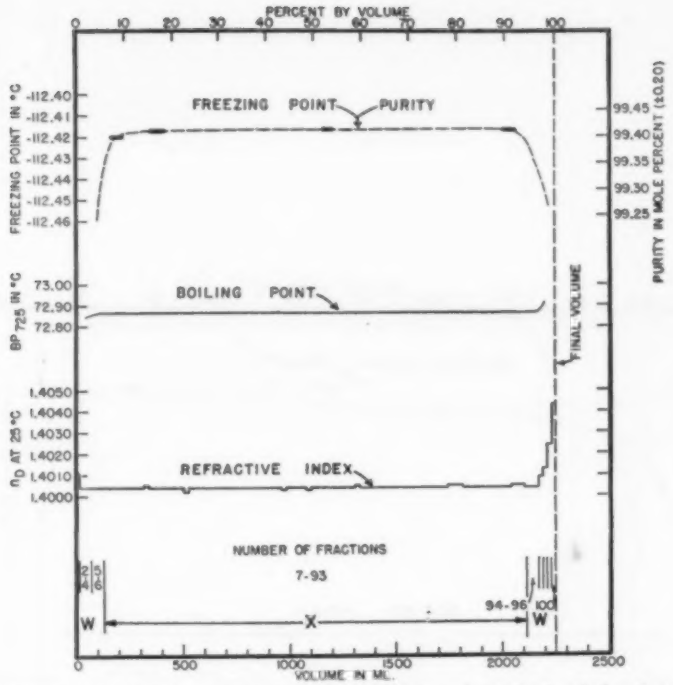

FIGURE 40.—*Results of the second distillation of 2,2,3-trimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 15 (1/3/45 to 1/29/45). See legend for figure 39.

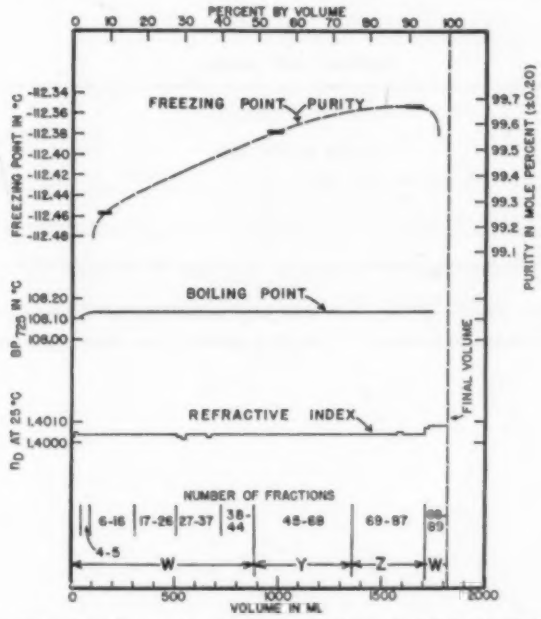

FIGURE 41.—*Results of the third distillation of 2,2,3-trimethylpentane.*

Regular distillation at 725 mm Hg in still 4 (2/14/45 to 3/2/45).

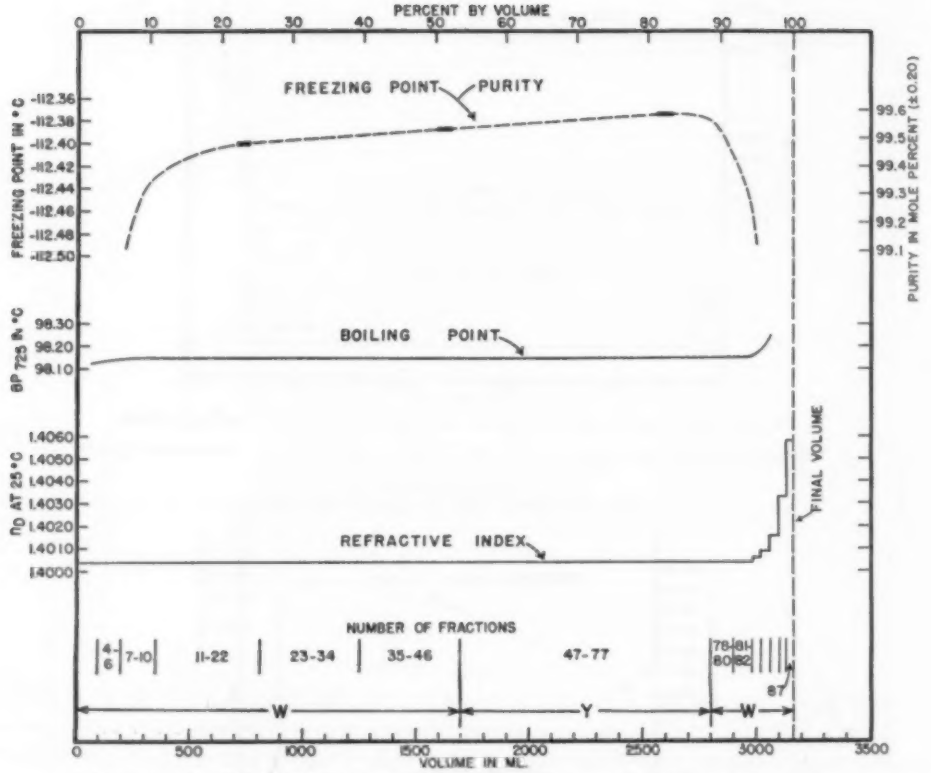

FIGURE 42.—*Results of the fourth and final distillation of 2,2,3-trimethylpentane.*

Azeotropic distillation with ethylene glycol monomethyl ether at 725 mm Hg in still 15 (2/16/45 to 3/5/45). See legend for figure 39 and footnote "j" of table

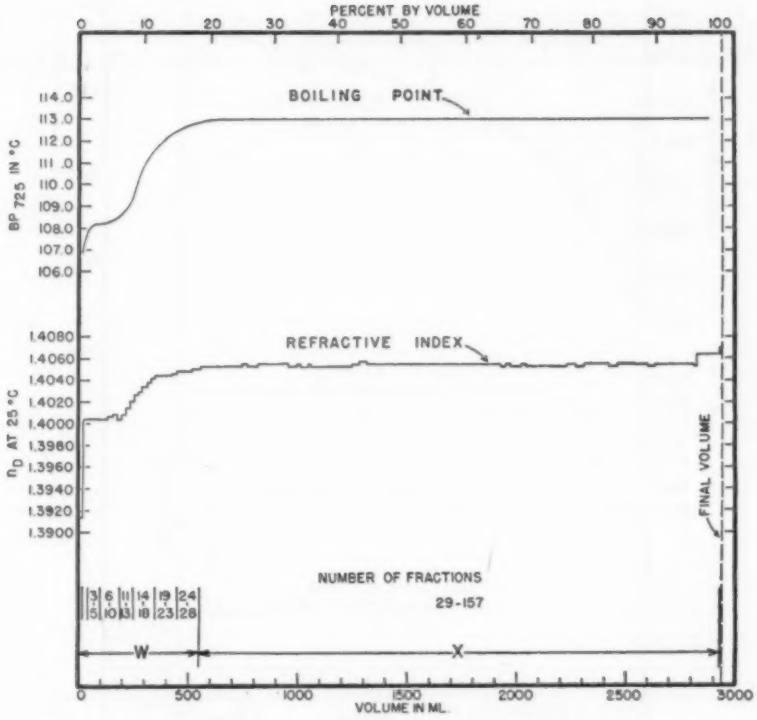

FIGURE 43.—*Results of the first distillation of 2,3,3-trimethylpentane.*

Regular distillation at 725 mm Hg in still 9 (11/27/44 to 12/26/44).

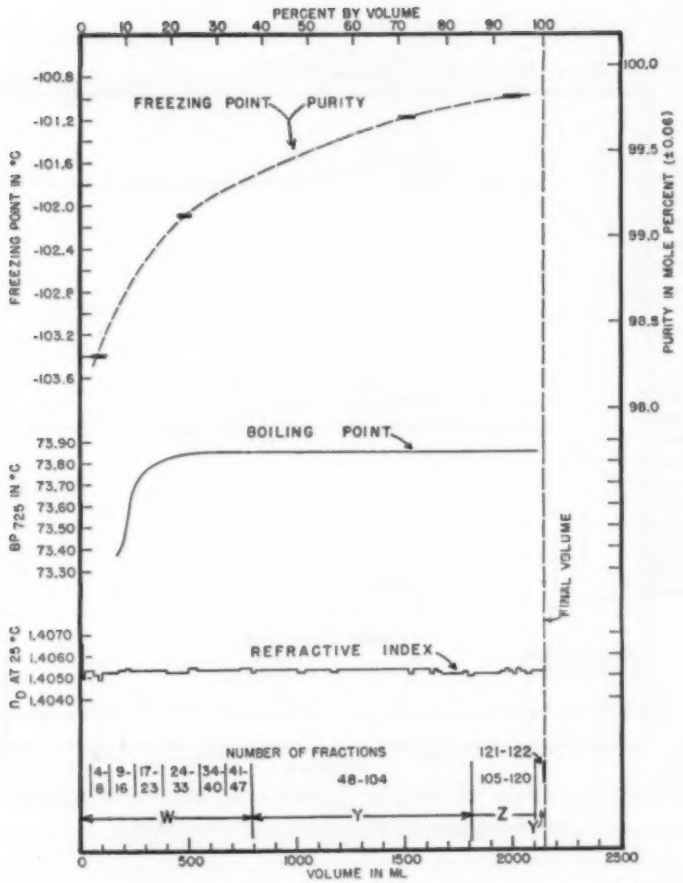

FIGURE 44.—*Results of the second and final distillation of 2,3,3-trimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 8 (1/8/45 to 2/5/45).

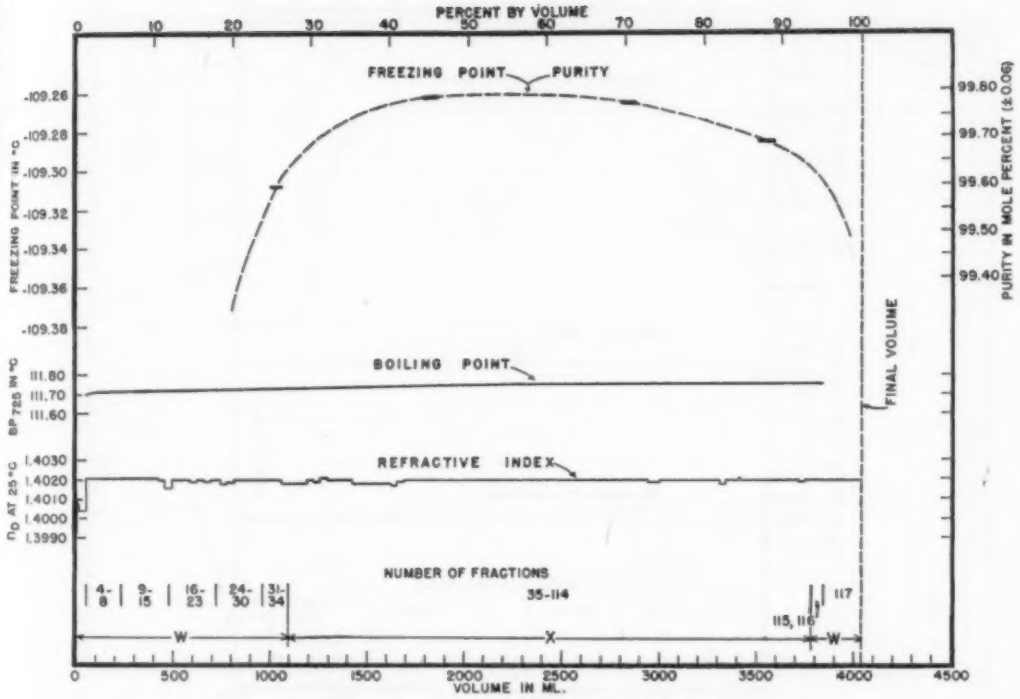

FIGURE 45.—*Results of the first distillation of 2,3,4-trimethylpentane.*

Regular distillation at 725 mm Hg in still 7 (8/28/44 to 9/19/44).

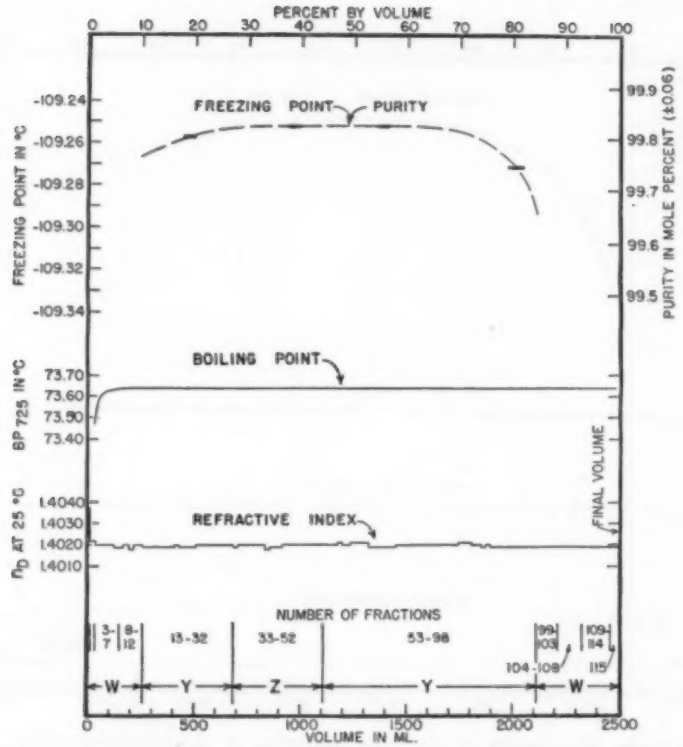

FIGURE 46.—*Results of the second and final distillation of 2,3,4-trimethylpentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 14 (12/27/44 to 1/18/45).

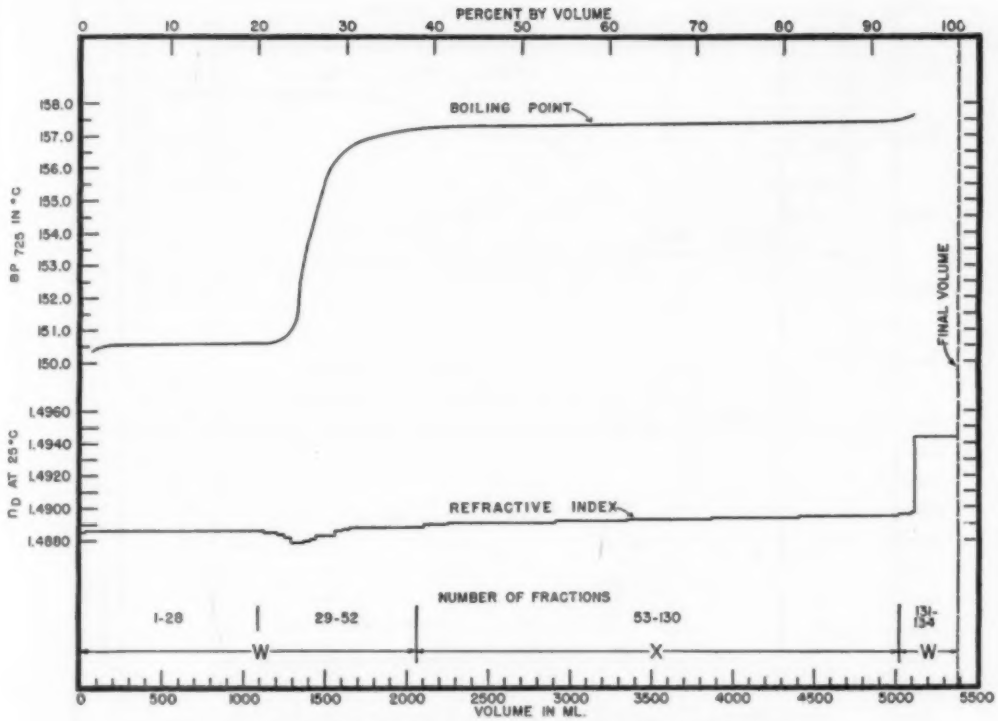

FIGURE 47.—*Results of the first distillation of n-propylbenzene.*

Regular distillation at 726 mm Hg in still 8 (5/23/44 to 6/20/44). This is one of two similar distillations.

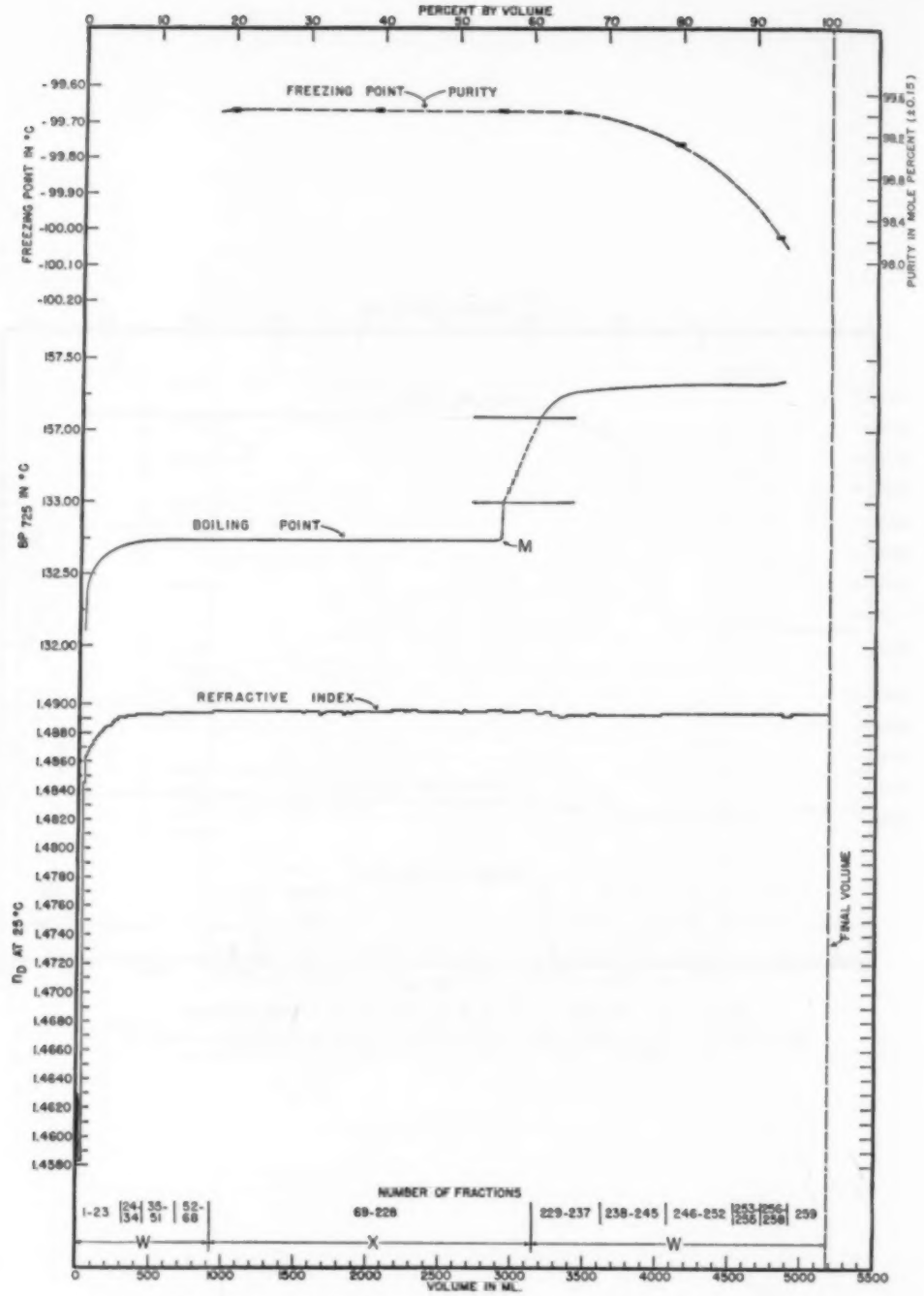

FIGURE 48.—*Results of the second distillation of n-propylbenzene.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 5 (9/5/44 to 10/21/44). See footnote "m" of table 1. At the point marked "*M*" the azeotrope-forming substance was exhausted and the remainder of the distillation was regular.

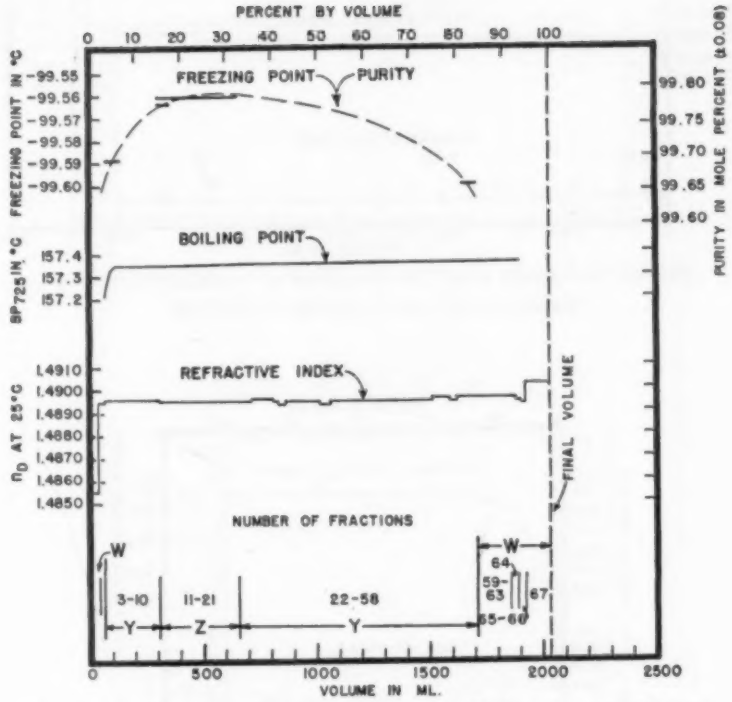

FIGURE 49.—*Results of the third and final distillation of n-propylbenzene.*

Regular distillation at 725 mm Hg in still 13 (12/23/44 to 1/8/45).

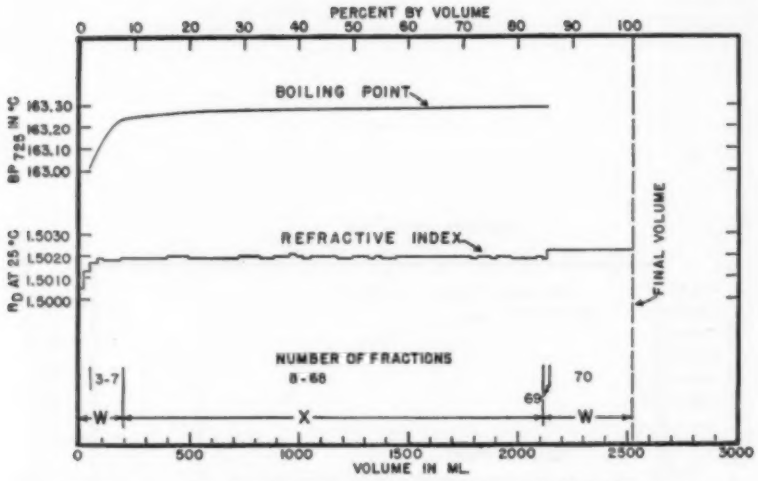

FIGURE 50.—*Results of the first distillation of 1-methyl-2-ethylbenzene.*

Regular distillation at 725 mm Hg in still 7 (5/5/44 to 5/21/44).

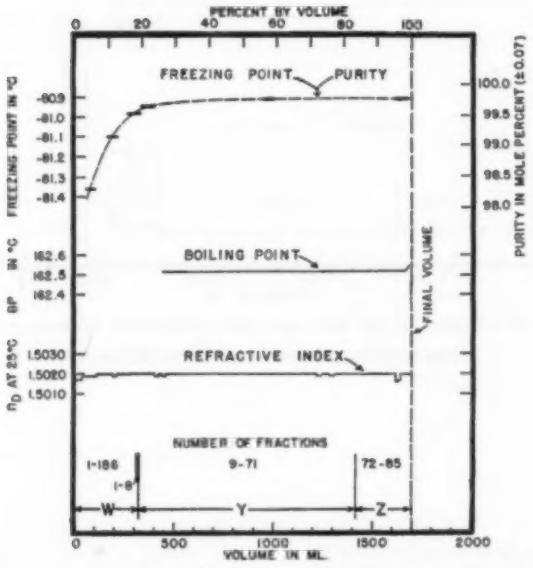

FIGURE 51.—*Results of the second and final distillation of 1-methyl-2-ethylbenzene.*

Azeotropic distillation with ethylene glycol monoethyl ether and diethylene glycol monomethyl ether at 725 mm Hg in still 4 (6/26/44 to 8/15/44). Fractions 1 to 186 in the portion marked "W" represent the hydrocarbon which distilled with ethylene glycol monoethyl ether. The remainder of the hydrocarbon was distilled with diethylene glycol monomethyl ether (see footnote "n" of table 1).

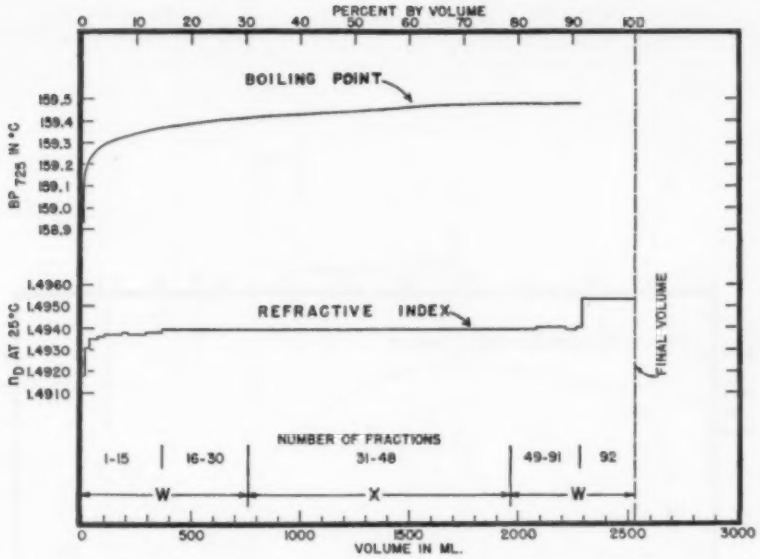

FIGURE 52.—*Results of the first distillation of 1-methyl-3-ethylbenzene.*

Regular distillation at 725 mm Hg in still 8 (3/17/44 to 3/30/44).

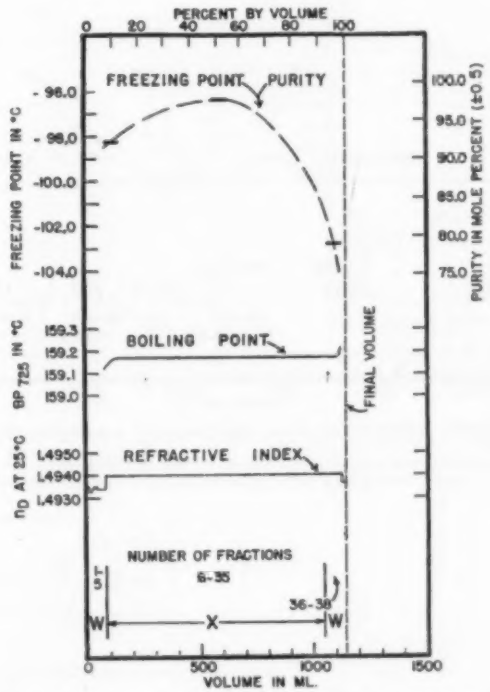

FIGURE 53.—*Results of the second distillation of 1-methyl-3-ethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 8 (4/11/44 to 4/24/44).

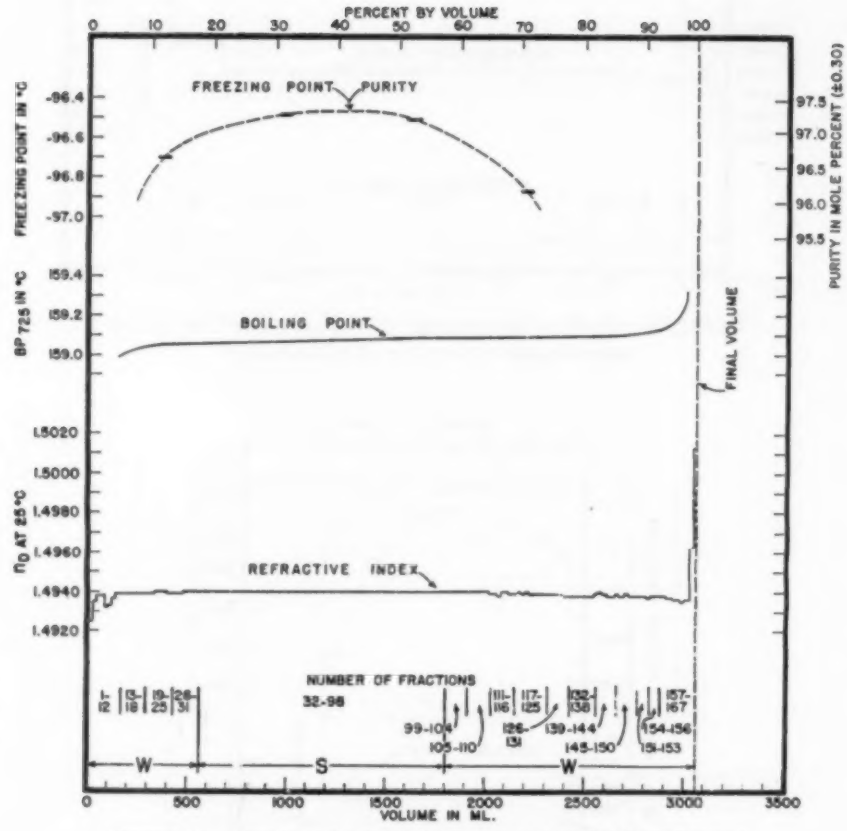

FIGURE 54.—*Results of the third distillation of 1-methyl-3-ethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 9 (10/2/44 to 11/1/44). See footnote "o" of table 1. The portion of the distillate marked "*S*" was purified further by sulfonation and hydrolysis (see fig. 55 and footnote "p" to table 1).

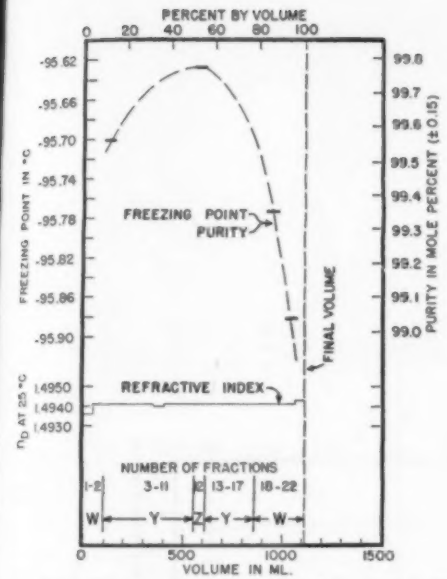

FIGURE 55.—*Results of final purification of 1-methyl-3-ethylbenzene by sulfonation and hydrolysis.*

See footnote "p" of table 1. (Purification performed 12/11/44).

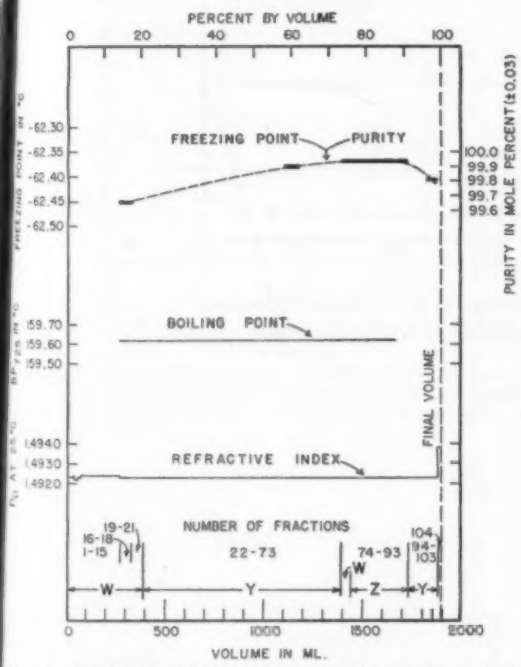

FIGURE 56.—*Results of first and only distillation of 1-methyl-4-ethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 12 (9/28/44 to 10/21/44). 50 ml of fractions 74 to 93 was returned to the supplier as a "best" sample.

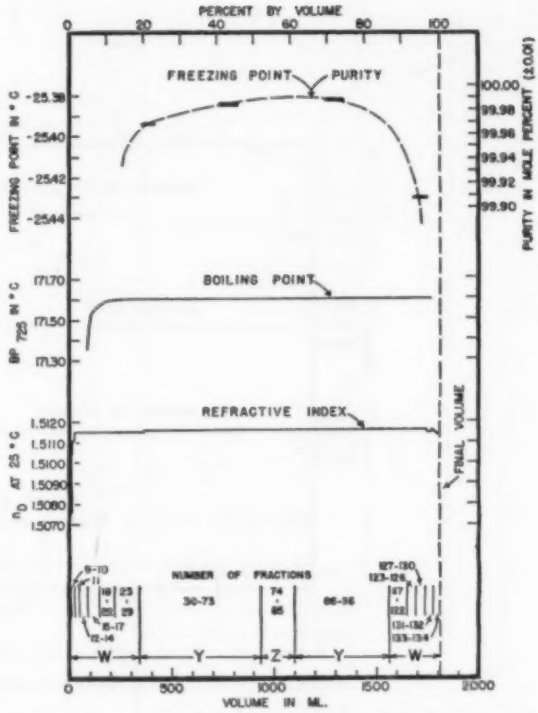

FIGURE 57.—*Results of first and only distillation of 1,2,3-trimethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 10 (4/24/45 to 5/18/45).

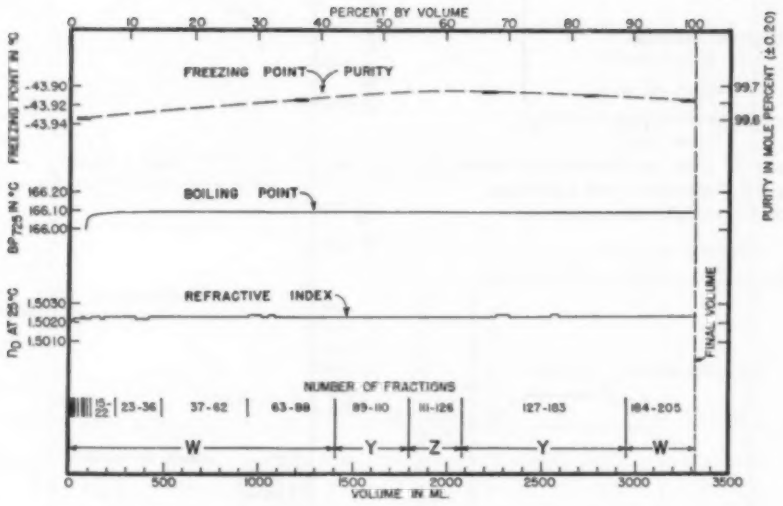

FIGURE 58.—*Results of first and only distillation of 1,2,4-trimethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 4 (9/29/44 to 11/4/44).

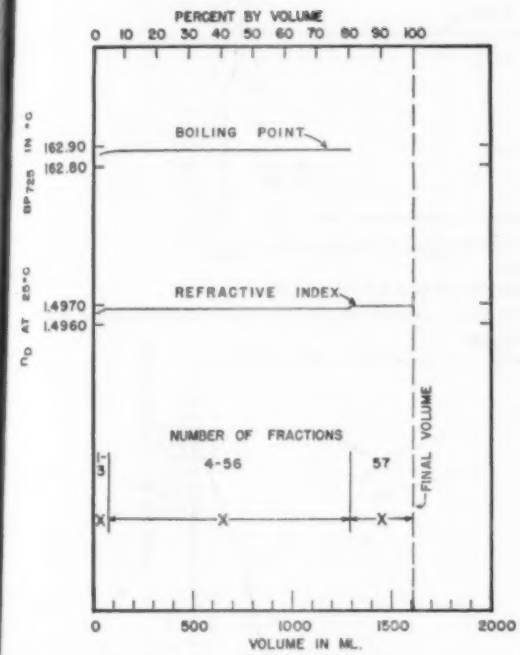

FIGURE 59.—*Results of the first distillation of 1,3,5-trimethylbenzene.*

Regular distillation at 725 mm Hg in still 8 (3/6/44 to 3/16/44). Fractions 1 to 3 and 57 were included in the charge for the third distillation of this hydrocarbon (see figure 61) and fractions 4 to 56 were redistilled in the second distillation (see figure 60).

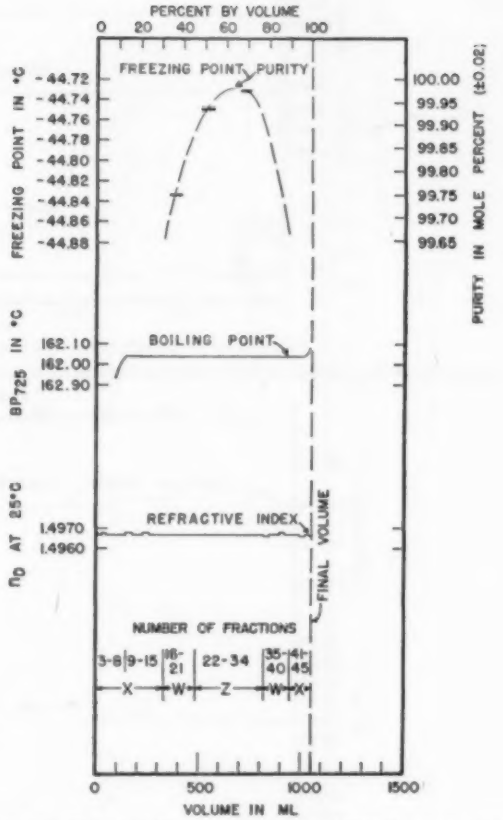

FIGURE 60.—*Results of the second distillation of 1,3,5-trimethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 8 (5/12/44 to 5/22/44). See legend for figure 59.

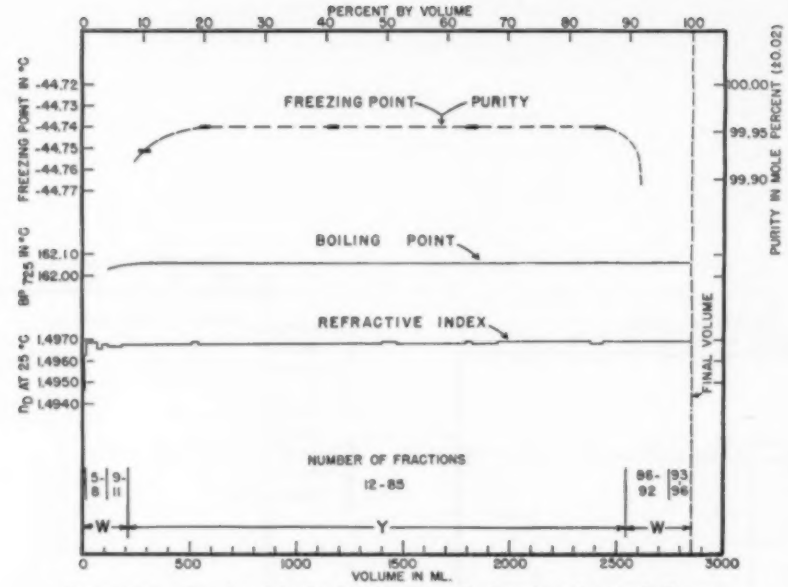

FIGURE 61.—*Results of the third and last distillation of 1,3,5-trimethylbenzene.*

Azeotropic distillation with diethylene glycol monomethyl ether at 725 mm Hg in still 8 (9/12/44 to 9/30/44). See legend for figure 59 and footnote "g" of table 1.

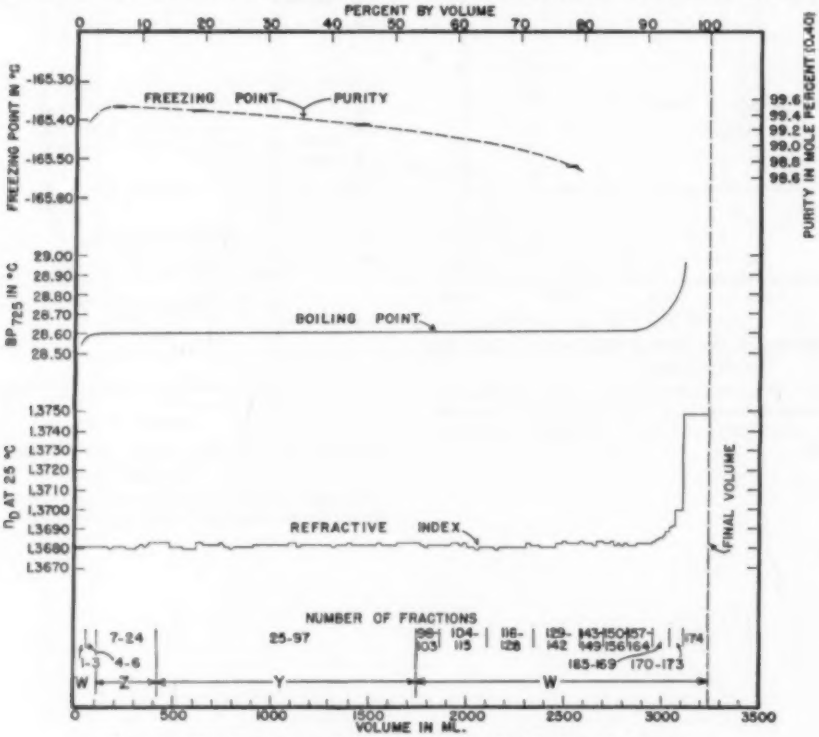

FIGURE 62.—*Results of the first and only distillation of 1-pentene.*

Regular distillation at 725 mm Hg in still 4 (1/9/45 to 2/12/45).

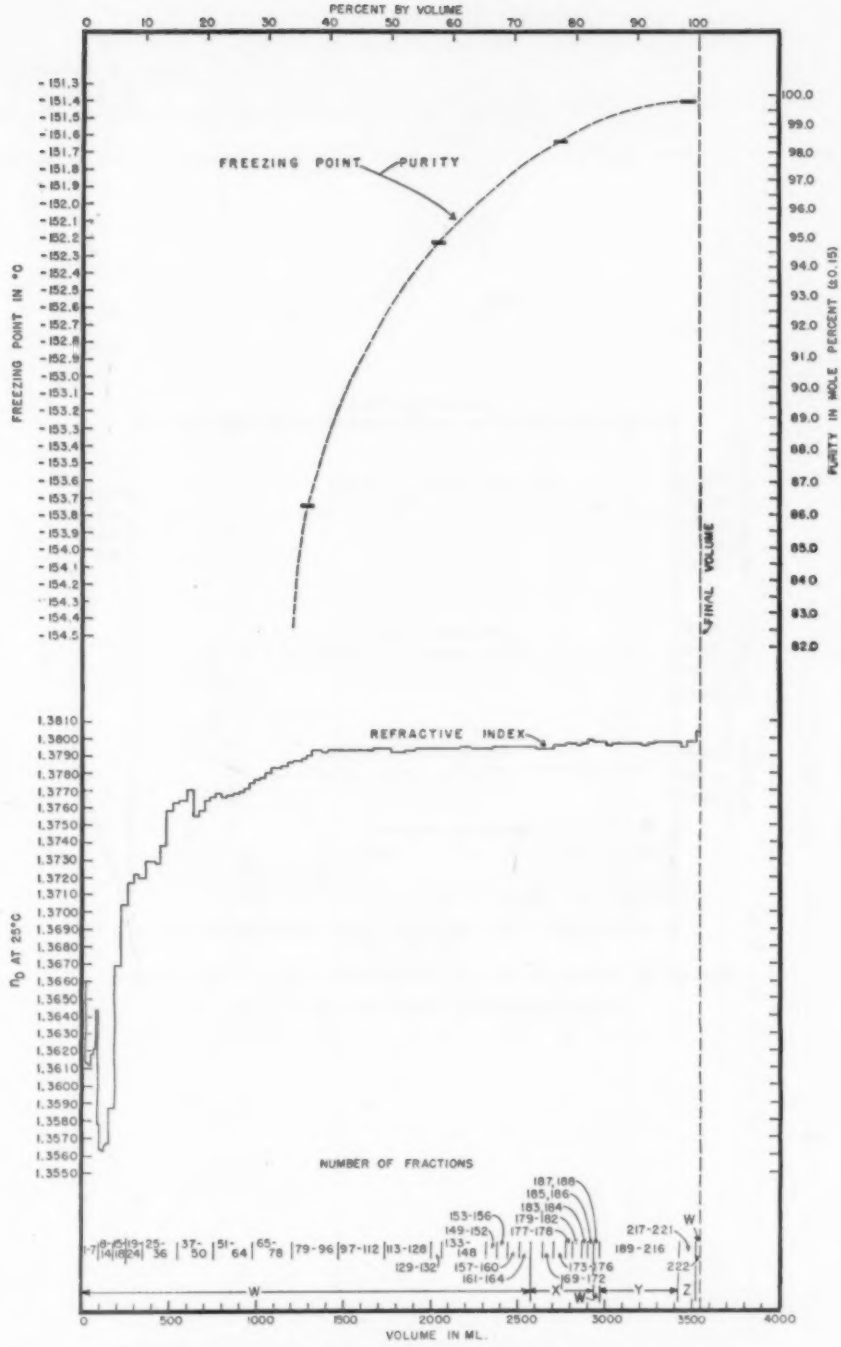

FIGURE 63.—*Results of the first and only distillation of cis-2-pentene.*

Azeotropic distillation with methanol at 725 mm Hg in still 4 (7/16/45 to 9/29/45). The portion maked "X" was retained for further processing by the API Research Project 6.

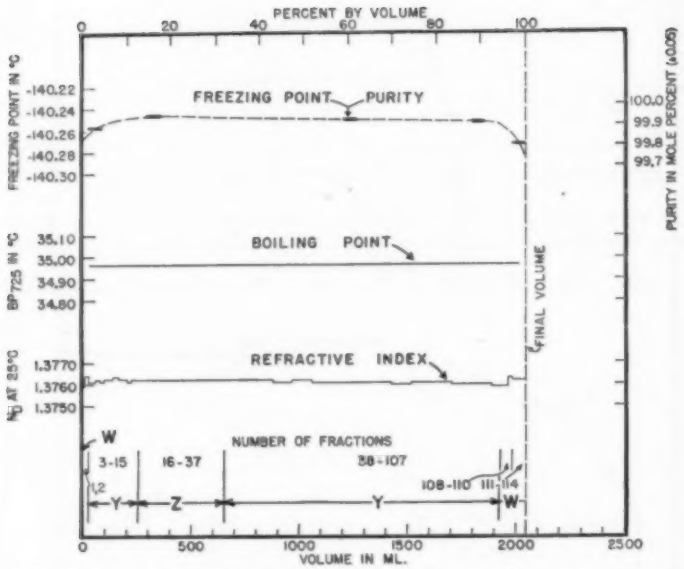

FIGURE 64.—*Results of the first and only distillation of trans-2-pentene.*

Regular distillation at 725 mm Hg in still 1 (2/3/45 to 3/16/45).

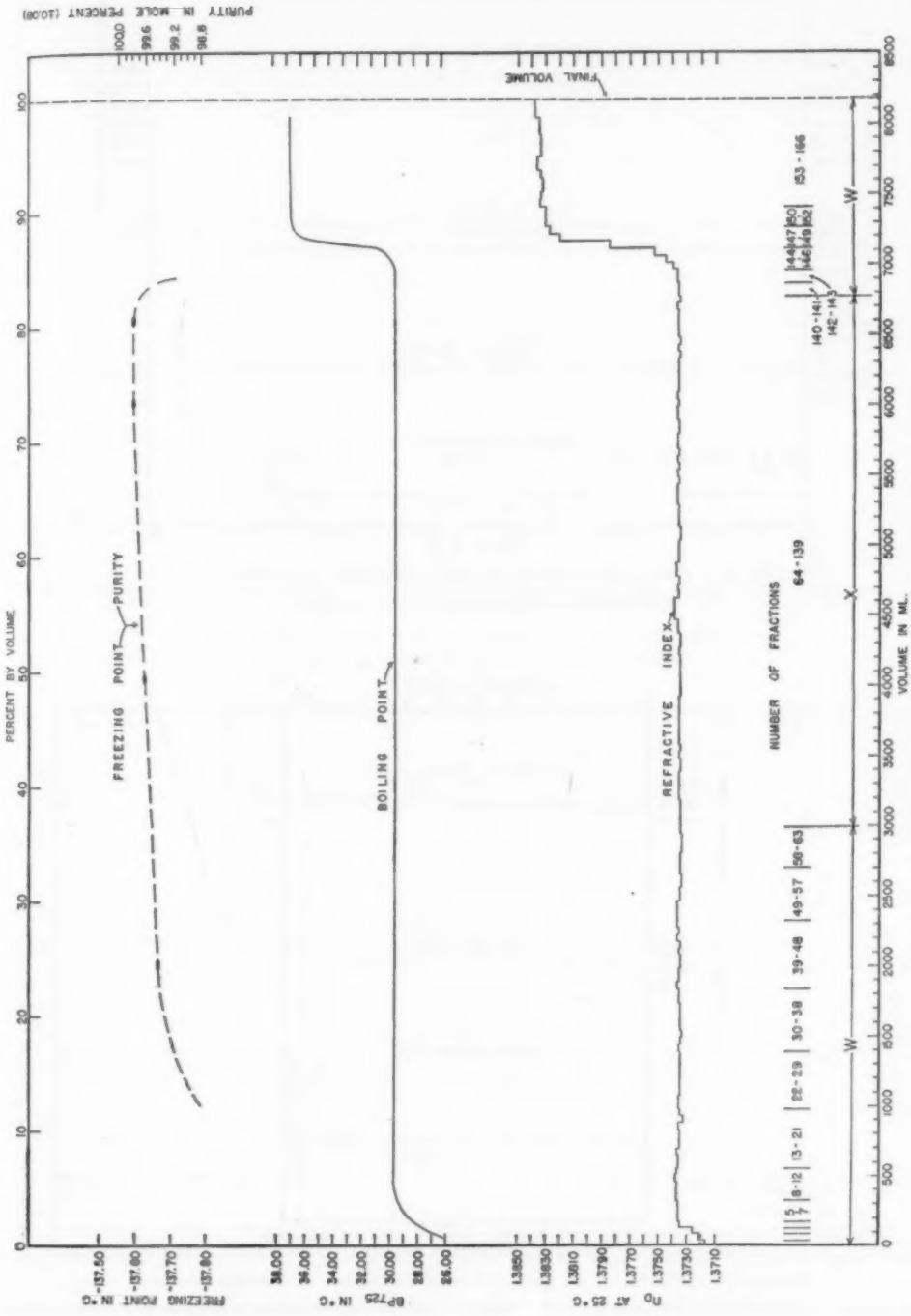

FIGURE 65.—*Results of the first distillation of 2-methyl-1-butene.*

Regular distillation at 725 mm Hg in still 5 (12/8/44 to 1/12/45).

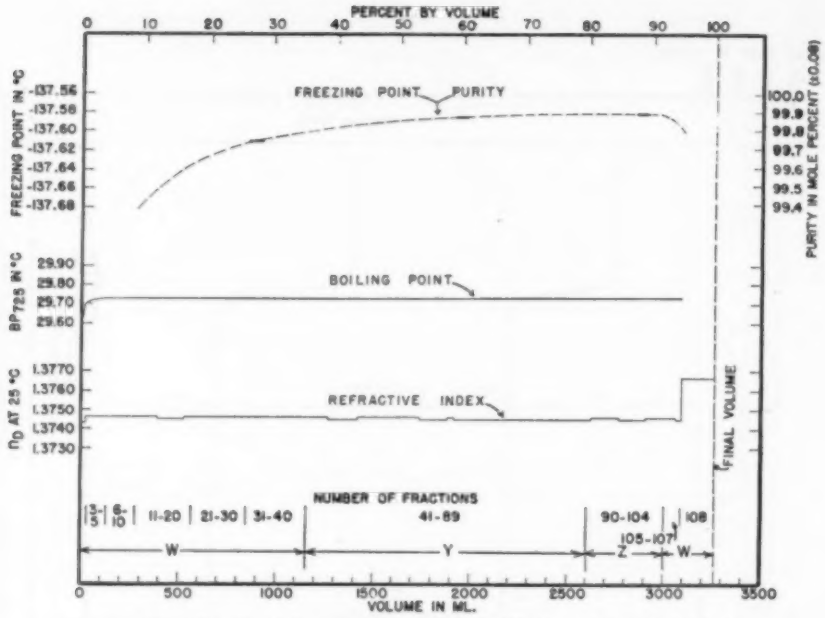

FIGURE 66.—*Results of the second and final distillation of 2-methyl-1-butene.*

Regular distillation at 725 mm Hg in still 13 (2/7/45 to 3/5/45).

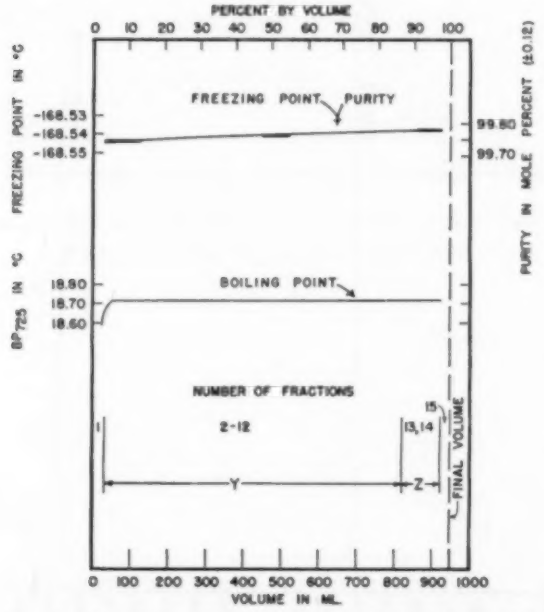

FIGURE 67.—*Results of the first and only distillation of 3-methyl-1-butene.*

Regular distillation at 725 mm Hg in still 1 (3/30/45 to 4/14/45). Fractions 1 and 15 were blended and used to determine the cryoscopic constant.

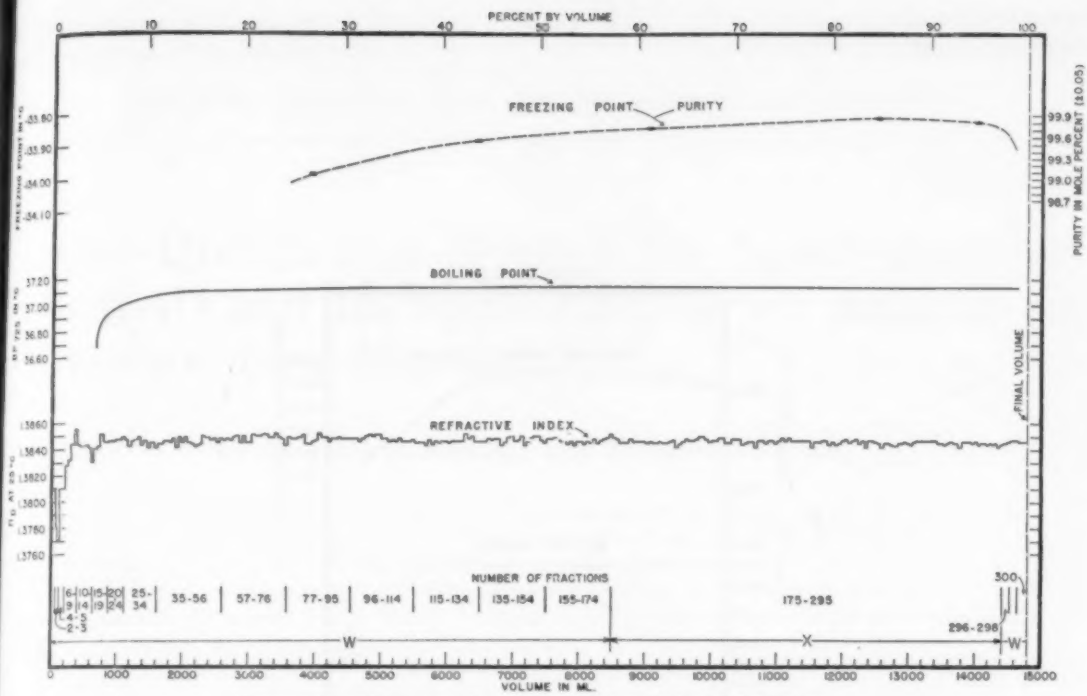

FIGURE 68.—*Results of the first distillation of 2-methyl-2-butene.*

Regular distillation at 725 mm Hg in still 6 (12/4/44 to 2/2/45).

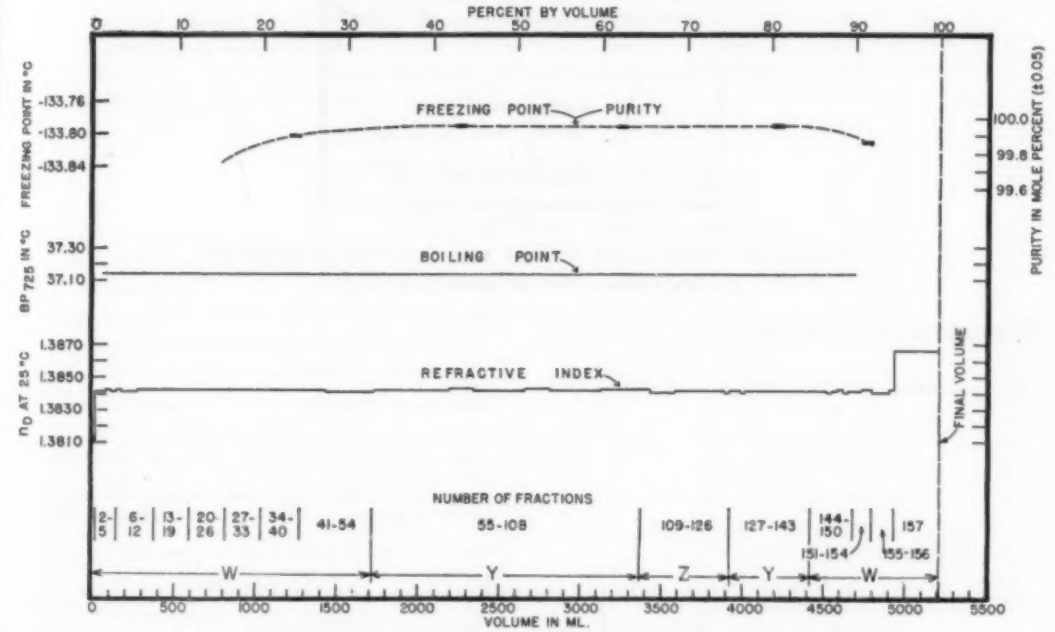

FIGURE 69.—*Results of the second and final distillation of 2-methyl-2-butene.*

Regular distillation at 725 mm Hg in still 8 (3/1/45 to 4/5/45).

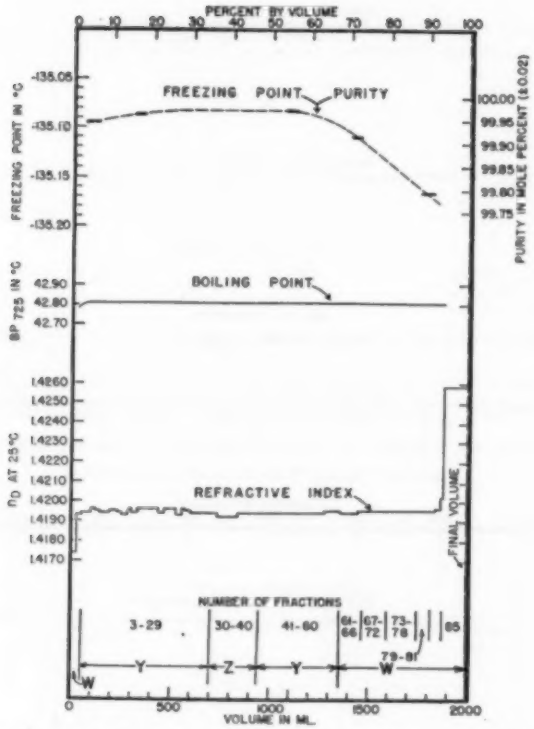

FIGURE 70.—*Results of the first and only distillation of cyclopentene.*

Regular distillation at 725 mm Hg in still 12 (4/6/45 to 5/14/45).

WASHINGTON, June 15, 1946.

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Carrier-Distillation Method for Spectrographic Analysis and Its Application to the Analysis of Uranium-Base Materials[1,2]

By Bourdon F. Scribner and Harold R. Mullin

A method of fractional distillation in the direct-current arc was developed for the spectrographic determination of 33 volatile impurity elements at concentrations as low as a fraction of a part per million in uranium-base materials. The method involves (1) the conversion of the sample matrix to a form having low volatility, (2) the addition of a small amount of a selected volatile "carrier" material, and (3) partial distillation of the mixture in a direct-current arc with an electrode assembly of improved design. In the analysis of uranium-base materials, the sample was converted to the oxide U_3O_8 and gallium oxide was added as a carrier (2 parts Ga_2O_3, 98 parts U_3O_8). The procedure was applied to the determination of Ag, Al, As, Au, B, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Ge, Hg, In, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Si, Sn, Tl, V, and Zn. Repeated results for B, Cd, Si, Fe, Mg, and Mn, determined photometrically, agreed within ±10 percent. The high sensitivity and general applicability of the method are results of the characteristic that the refractory sample matrix is not volatilized appreciably, during the period that the minute quantities of impurity vapors are swept into the arc by the carrier.

I. Introduction

The factors entering into the utilization of uranium as a source of atomic energy have been discussed by Smyth [1].* One of the limitations in attaining a nuclear chain reaction lies in nonfission capture of neutrons by impurities. The impurities differ in this absorptive power, but

*Figures in brackets indicate the literature references at the end of this paper.

[1] This investigation was sponsored by the Office of Scientific Research and Development and by the Manhattan Project. The information covered in this document will appear in Division VIII of the Manhattan Project Technical Series, as part of a contribution of the National Bureau of Standards.

[2] Presented at the meeting of the Optical Society of America on March 8, 1946.

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certain common elements such as boron, lithium and cadmium are particularly effective. It had been shown by calculations that many impurities should not exceed a few parts per million and, in the case of the highly absorbing elements, freedom even from a few tenths parts per million was desirable. Impurities also have a deleterious but less-pronounced effect on the metallurgical properties of uranium metal. The production of uranium, to be used as a source of atomic energy, consequently involves a most searching analysis into the composition of the intermediate and final products. Methods were required for the determination of 60 or more chemical elements in a variety of uranium-base materials with speed, high-sensitivity, and sufficient accuracy as important considerations.

Early in 1941 this laboratory began an investigation of the applicability of spectrographic methods to this analytical problem. The principal obstacle encountered was the interference of the uranium spectrum with the spectral lines of the elements to be determined. Uranium is characterized by complex spectra derived from a multiplicity of electron configurations in both the neutral and ionized atoms. The spectra of different stages of ionization are difficult to isolate because of the low ionization potential of uranium, which is approximately 4 volts [2]. The rich line-spectrum is further confused by a heavy background contributed by unresolved weak lines and by the continuous radiation of solid particles, a characteristic that is common to elements forming refractory oxides. Because of these properties little simplification could be realized by a choice between the usual excitation methods; furthermore, recourse to very high spectral dispersion appeared impracticable. It was apparent that sensitive spectrographic methods of general utility could be developed only by suppressing or otherwise avoiding the spectra of uranium atoms.

As a means of eliminating interference by the spectrum of uranium, fractional distillation in the d-c arc appeared promising. It is a well-known fact that the constituents of a sample undergoing excitation for spectral study may distill at different rates, depending on their volatilities. This is particularly true in excitation by the d-c arc when the sample is contained in a cupped graphite electrode which acts much like a small furnace. In 1918 Mott [3] applied arc distillation phenomena in studying the volatilities of refractory materials, and in 1920 he suggested [4] the use of arc images to observe the volatilization of various constituents as a means of chemical analysis. Fractional distillation was later applied in spectrographic analysis by Rubies [5, 6], by Preuss [7] and others.

The application of simple fractional distillation was found unsatisfactory in view of the requirements for complete suppression of the uranium spectrum and for accurate control of excitation to permit quantitative determination of impurities. Variations in the chemical form of the uranium-base sample, in its physical properties, and in total impurity content markedly affected the results. The problem lay in developing a means of distillation and excitation whereby trace impurities could be removed from the uranium matrix and their spectra recorded under conditions suitable for quantitative determination.

An investigation of the problem led to the development of a modified method of fractional distillation involving (a) conversion of the sample matrix to a form having low volatility, (b) addition of a small amount of a selected volatile "carrier" material, and (c) partial distillation of the mixture in a d-c arc under carefully controlled conditions. The method was first applied in 1942 to the determination of boron in uranium-base materials. It was subsequently extended, by the choice of suitable wavelengths and by the preparation of standards, to cover the determination of 33 volatile impurities. The limit of detection for the majority of the elements is a few parts per million, although, for important cases, the sensitivity was extended to less than 0.1 ppm. The degree to which uranium interference is avoided by this method, with resulting high sensitivity of detection of impurities, is exhibited in figure 1. Exposures *A* (direct burning) and *B* (carrier-distillation method) were made with a sample containing 500 ppm of Al and Fe, and 50 ppm of Cu. Exposure *C* (carrier-distillation method) represents a sample containing 50 ppm of Al and Fe, and 5 ppm of Cu. The method is generally applicable, with minor modifications and the proper standard samples, to the analysis of other refractory materials. The conditions under which the method is applied have a considerable bearing on its success, and these will be examined in detail.

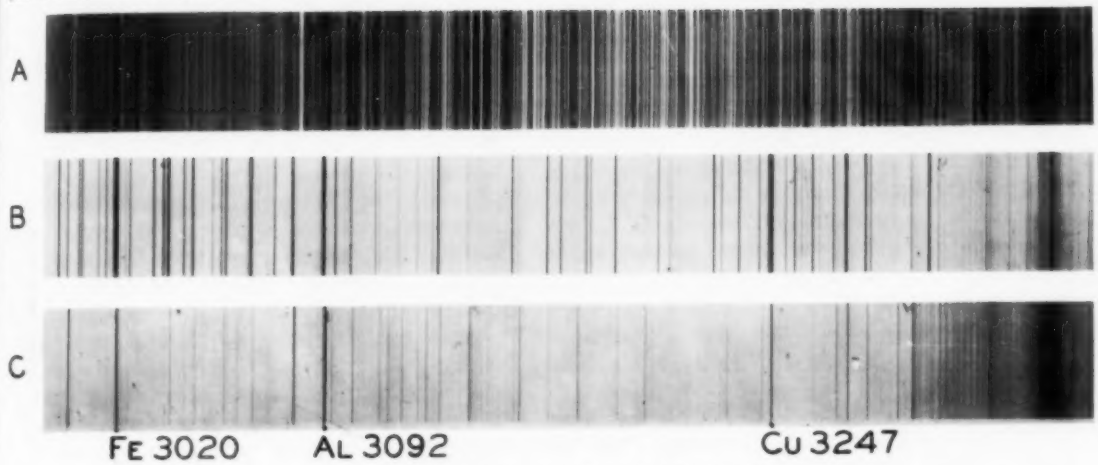

FIGURE 1.—*Arc spectrograms in the region 3000 to 3350 A.*

A, Spectrum of 1 mg of U_3O_8 by direct arcing; *B*, spectrum obtained from 100 mg of U_3O_8 by the carrier-distillation method; *C*, same as *B*, except that the uranium sample is of higher purity.

UNIV. OF MICH.

II. Discussion

1. The Carrier and Its Function

In studies of simple fractional distillation in the arc, a variety of uranium compounds of different degrees of purity were examined. Observing that the sensitivity of detection of a trace impurity was enhanced in the presence of other impurities, we investigated the effect of various additions to the uranium sample. In general, a marked increase in the sensitivity of volatile impurities was observed. Added materials of intermediate volatility were most effective, and conditions could be so adjusted that the volatile impurities would distill with the carrier, but only a trace of the uranium would be carried into the arc. The principal function of the added material, or "carrier", is to sweep out slowly the minute quantities of impurities volatilized by the heat of the electrode, thereby effecting a sharp separation from the more refractory matrix. At the same time, the carrier supports and stabilizes the arc.

The choice of a carrier involves certain limitations, but it may be expected that several materials will provide satisfactory results. However, salts such as ammonium chloride and sulfate were too volatile and, even in small amounts, introduced uranium into the arc. Alkali salts tended to suppress boron lines, possibly because of the depressing effect of the low ionization potential of the alkali metal in the arc. In general, the carrier should have an intermediate volatility and an intermediate ionization potential among the group of elements to be determined, be free of those elements, be stable, inert, nonhygroscopic and easily incorporated in the samples by grinding. In the analysis of uranium-base materials, where determinations of many elements were desired, the choice of a carrier narrowed down to an element of minimum importance, one that is not a common or critical impurity in the samples. Pure gallium oxide, one of the first materials tested as a carrier, satisfied the requirements and has been employed extensively for this purpose within the project. As gallium was readily determined in a chemical concentrate obtained for a supplementary spectrographic procedure, it was not necessary to consider its determination by the carrier-distillation method. Harrison and Kent [8] have recommended silver chloride as a possible substitute for gallium oxide.

Gallium oxide of the requisite purity was prepared by a procedure suggested by Hoffman and involving an ether separation which he has described [9]. Gallium metal is partially dissolved in hydrochloric acid, leaving a residue of 5 to 10 percent of the metal. The elements less active than gallium tend to concentrate in the residue, and in most instances this procedure suffices for purification. If necessary, an ether extraction may be made for further purification, and then the chloride is converted to oxalate, which finally is ignited to oxide at 1,200° C.

The selection of the concentration at which the carrier is added to the sample is based upon the amount required to sweep out the impurities and to maintain a steady arc for a sufficient length of time for reasonable exposure of the photographic plate. The upper limit on the amount added is determined by the tendency of excessive amounts to carry particles of the uranium sample mechanically into the arc stream. The choice of a ratio of 2 parts of gallium oxide (Ga_2O_3) to 98 parts of uranium oxide (U_3O_8) has proved satisfactory. The dense form of gallium oxide, obtained by ignition at 1,200° C, is preferred for ease in weighing and transferring. The carrier is incorporated in the uranium oxide by hand-grinding in a small mortar.

2. Arc Excitation

The form and dimensions of the arc electrode assembly have important effects on the rate and degree of heating of the charge. The electrode combination employed, figure 2, is similar to that described by Scribner and Corliss [10], but it provides a deep cup in the anode in which the sample charge is heated. A further modification is the tapered fit between the cap and pedestal, providing accurate alinement of the electrode. The two-piece anode minimizes heat conduction from the anode cap, resulting in a high temperature and only moderate gradient from top to bottom of the cap. The charge thus is exposed to relatively uniform heating from the electrode wall, while direct contact with the arc stream is avoided. Prior to excitation, a charge of 100 mg of the sample mixture (98 parts of U_3O_8 and 2 parts of Ga_2O_3) is transferred to the electrode, which is

mounted in an electrode block. The electrode is tapped to distribute the charge evenly, and a vent hole is made vertically through the center of the charge. The vent serves to release gases that otherwise may cause ejection of the charge into the arc stream when the arc is struck.

The arc excitation of the samples is characterized by a cycle of burning that is quite reproducible for the purer grades. The electrodes are mounted as shown in figure 2, with a separation of 4 mm, and a 10-ampere arc is struck. The arc burns somewhat erratically for about 10 seconds, being supported mainly by volatilization of the electrode material. At the end of this period the arc changes in color from indigo to blue and runs quietly and steadily for approximately 25 seconds,

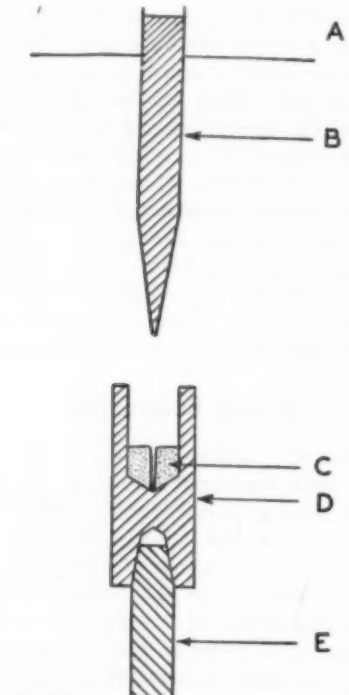

FIGURE 2.—*Electrode assembly.*

A, Holder; *B*, cathode; *C*, sample charge; *D*, anode; *E*, pedestal.

changing at this point to the unsteady condition of the initial period. Studies by the moving-plate technic have shown that the steady period results from distillation of the carrier and the greater part of the volatile impurities into the arc stream. However, certain highly volatile impurities, such as cadmium and mercury, begin to volatilize ahead of the steady period, and elements such as aluminum and magnesium, present as refractory oxides, persist in the arc at the end of the steady period. During the volatilization of the gallium only a trace of the uranium is removed, and the spent charge may be set aside for recovery of the uranium.

Spectrographic analysis of the burned charges, made by repeating the procedure with a new portion of the carrier, has shown that the end of the steady period does not represent complete volatilization of even the more volatile elements. This is a necessary result of the restriction that the temperature must be kept below the limit at which the charge fuses and uranium is evolved. Observation of the burning electrode with an optical pyrometer showed that the outer surface reached a temperature of 2,800° C near the top of the electrode and 2,300° C near the bottom. The charge, heated by radiation from the interior wall of the electrode, sinters to a fragile cake but does not melt, which indicates that the temperature is slightly below the melting point of U_3O_8. The working temperature, estimated to be in the neighborhood of 2,000° C, is below the boiling point or decomposition temperature of many of the impurity oxides; volatilization probably depends on their vapor pressures at the charge temperature. For most of the elements (gold is an exception), the volatility can be considered proportional to the boiling point of the oxide.[3] The behavior of the impurities suggests a division into three groups in which the oxides have boiling points (a) below 1,500° C, (b) around 2,000° C, and (c) in the neighborhood of 3,000° C. Impurities in the first group volatilize rapidly and nearly completely; those in the second group volatilize more slowly, resembling gallium oxide in behavior; those in the third group volatilize less completely, and the degree of volatilization is more severely affected by variations in the heating conditions.

[3] The two papers by Mott [3, 4] contain much useful information on relative boiling points of elements and their compounds.

The behavior of the first two groups of impurities permits satisfactory spectrographic determination by visual and photometric interpolation against standard samples handled in the same manner. For example, boron is determined by preparing an analytical curve, figure 3, in which log intensity of the boron line is plotted against log

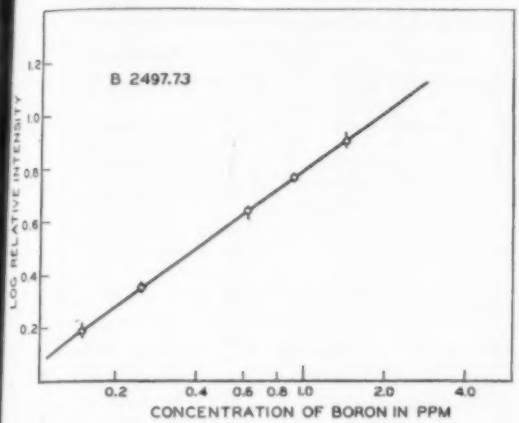

FIGURE 3.—*Analytical curve for the determination of boron.*

concentration of boron for a series of standard samples, each point representing four observations. Subsequent boron determinations are made by similar measurements on unknown samples and a reference standard on the plate, the log I values are corrected to bring the reference standard into agreement with the curve, and the boron determinations are read from the curve.

For accurate determination of elements of the third, or low-volatility, group, the addition of an internal-control element was found necessary. In this case the intensity of the impurity line was measured relative to that of an added element which behaves similarly in volatilization. The determinations of iron, magnesium, and manganese, falling in this group, were made by photometric measurement relative to chromium added in the gallium oxide carrier (Ga_2O_3 containing 1 percent of Cr as Cr_2O_3). An analytical curve for the determination of iron is shown in figure 4.

Consideration of volatility is also important in adjusting exposure times in the analytical procedures. For second- and third-group elements, a portion of the initial burning period can be omitted from the exposure without appreciable error; this is useful in some cases in reducing spectral background. For the first-group elements, which begin to volatilize almost immediately, the exposure is begun the moment the arc is struck, but the total exposure may be cut short if necessary, as in the case of determination of cadmium, to reduce background.

This discussion of excitation characteristics has assumed application to the purer grades of uranium-base materials. If the total content of volatile impurities in a sample rises toward 1 percent, the steady burning period will be longer. In these cases the results may be affected by the high concentration of volatile materials. Dilution of the impure sample by pure oxide (U_3O_8) serves to obviate these effects, and the diluted sample may be analyzed according to the basic procedure for pure oxide, the results being corrected by the dilution factor. The conversion of uranium salts to uranium oxide prior to application of the method should be complete to avoid any volatilization of uranium; erratic behavior in arc distillation in several cases has been traced to incomplete conversion.

The ignition of a uranium-base material will result in loss of mercury. Furthermore, the con-

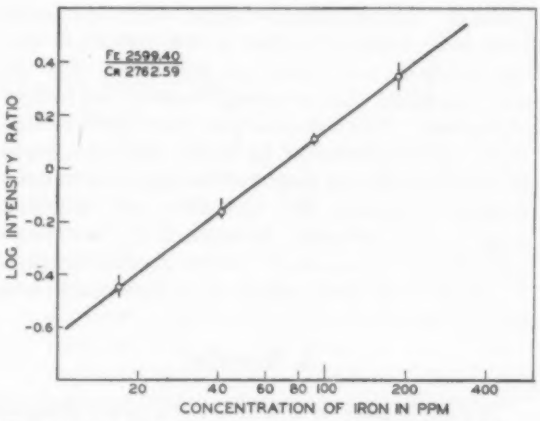

FIGURE 4.—*Analytical curve for the determination of iron.*

version of salts such as the fluoride (UF_4) may result in loss of boron and other elements having volatile fluorides. In these cases a separate examination of the original sample may be made for the elements in question, employing a modified carrier distillation procedure. Further details concerning special problems of this type are given in the experimental procedures.

3. Standard Samples

The ultimate success of the method depends not only on excitation controls but on the availability of standard samples having concentrations and excitation behavior matching those of the samples to be analyzed. To obtain comparable behavior in volatilization, the samples and standards should be matched as closely as possible in density, and in the chemical forms of the matrix and of the impurities; volatile anions should be avoided. One of the difficult problems encountered was that of obtaining sufficiently pure material for a standard matrix. The materials found purest by spectrographic test usually contained traces of B, Cu, Ag, Mg, Si, and Fe, but in varying amounts. The difficulty in obtaining one lot of material free of all elements, and also the large number of impurities to be added, made it necessary to prepare several sets of standards. Series of standards were prepared, in general, by adding measured quantities of solutions of the impurity elements to weighed quantities (10 to 50 g) of ignited uranium oxide (U_3O_8) in platinum dishes. The solutions were prepared, as far as possible, with salts such as the nitrate which would convert to oxide on ignition. The additions of small volumes of solutions were made to the matrix in a manner so that the solution was absorbed completely by the uranium oxide, thus avoiding losses on the surface of the dish. The mixtures were then dried, ground in an agate mortar, and ignited at 800° C. Separate standards were prepared for the more volatile elements, mercury and cadmium, and the final ignition was omitted. As a check on the standards, duplicate sets were compared, and chemical determinations were obtained in important cases when possible.

4. Results

The application of this procedure to the analysis of uranium-base materials permits the determination of 33 impurities, with the limits of detection given in table 1. The limits are those observed in routine practice and do not necessarily represent the ultimate limit that may be obtained under the most favorable conditions. For example, conditions were adjusted for high sensitivity in the determination of cadmium and boron, but for an element, such as zinc, of lesser importance as a neutron absorber, special treatments that would add time-consuming complications were avoided. The sensitivities that were attained met the requirements for the determination of this group of elements in the inspection and control of the purity of uranium-base materials.

TABLE 1.—*Lower limit of routine spectrographic determination of impurities in uranium oxide*

Element	Concentration	Element	Concentration
	ppm		*ppm*
Ag	0.05	K	2
Al	5	Li	0.5
As	5	Mg	1
Au	0.3	Mn	1
B	.08	Mo	1
Ba	10	Na	0.5
Be	0.1	Ni	2
Bi	.5	P	50
Cd	.07	Pb	1
Co	1	Rb	1
Cr	3	Sb	10
Cs	8	Si	3
Cu	0.3	Sn	1
Fe	1	Tl	3
Ge	0.2	V	5
Hg	10	Zn	20
In	0.5		

The accuracy of the determinations by the method depends upon matching the excitation behavior of the samples and properly prepared standards, and upon the precision of the spectrographic measurements. Increased precision is provided by photometric measurement, but this advantage is offset by the additional time and labor required, which would be excessive if applied to all determinations. A compromise was adopted whereby the more important determinations were made by photometric measurement, and the remainder were estimated, usually within a factor of two, by visual comparison of the spectrograms of samples and standards. The reproducibility of determinations made for B, Cd, Si, Fe, Mg, and Mn by photometric measurement was found to be within ±10 percent except for values at the extreme limits of the measurable range. For example, on a sample of uranium oxide containing 1.20 ppm of boron, a series of 18 runs on 6 plates showed an average deviation of ±7.9 percent and an extreme deviation of 13 percent. Examples of repeated determinations of Fe, Mg, and Mn in uranium-base samples are given in table 2.

TABLE 2.—*Repeated spectrographic determinations, of impurities in uranium-base samples*

Sample No.	Element	Observation 1	2	3	4	5	Mean
				ppm			
	Iron	28	32	30	28	27	29
	Manganese	7	7	8	9	7	8
	Iron	30	33	30	28	30	30
	Magnesium	12	13	10	14	15	13
	Manganese	7	8	9	9	9	8
	Iron	108	110	104	111	106	108
	Manganese	14	13	12	12	14	13
	Iron	89	76	77	87	88	83
	Manganese	8	8	9	9	9	9
	Iron	76	79	69	68	.....	73
	Manganese	11	9	11	11	.....	10
	Iron	33	37	34	27	.....	33
	Magnesium	35	33	30	36	.....	33
	Manganese	10	8	8	9	.....	9

In view of the fact that the chemical determination of iron was considered quite reliable, it is of interest to compare routine results by the two methods on a typical set of uranium-base samples, as shown in table 3. The chemical determinations were made in the Bureau's Chemistry Division.

The carrier-distillation method was applied to the quantitative determination of 33 elements in various uranium-base materials of interest to the Manhattan Project. The materials included uranium metal, various oxides (UO_2, UO_3, UO_4, and U_3O_8), and salts (UF_4, UCl_4, UF_6, uranyl acetate and nitrate, and sodium uranate). In isolated cases when the method was extended to impure grades of samples or to a salt, such as sodium uranate, differing markedly from the available standards, the accuracy was adversely affected. In these cases qualitative results were reported as estimated ranges of concentration to a factor of 10. The great majority of analyses involved samples of high-grade uranium-base materials.

TABLE 3.—*Determinations of iron in uranium-base samples by routine spectrographic and chemical methods*

Sample No.	Spectrographic	Chemical	Sample No.	Spectrographic	Chemical
	ppm	*ppm*		*ppm*	*ppm*
151	28	41	161	38	35
152	32	35	162	77	74
153	33	32	163	41	41
154	149	154	164	83	79
155	31	32	165	34	36
156	26	32	166	19	24
157	110	139	167	34	34
158	83	70	168	26	31
159	35	35	169	41	34
160	33	31	170	38	42

III. Experimental Procedures

1. Apparatus

The relative simplicity of the spectrum obtained by the carrier-distillation method permits the use of spectographs of moderate dispersion, although for high sensitivity the reduction of spectral background with increased dispersion is an advantage. A commercial grating spectrograph, Eagle mounting, having a dispersion of 5.6 A per mm in the first order, is employed for the procedures to be described. A step sector (step ratio 2X, steps 2 mm high) and quartz lens (f_D=44 cm) are mounted at the secondary focus of the grating in the customary manner to focus an image of the arc source on the grating. By this means the sector intercepts a uniform beam of light and the spectral-line images appear as a pattern of exposures with the ratios of the exposures determined by the corresponding ratios of the opening in the step sector. The spectral line images then may be measured at optimum blackening values, and the line patterns may be employed for calibration of the plate. The usual facilities of a well-equipped spectrographic laboratory, including a direct-reading microphotometer, are sufficient for the work, although some additional minor equipment for preparation of samples and standards is required.

The minor equipment includes polished agate or mullite mortars, small balances designed for rapid weighing, drilled blocks for storing electrodes, and special tools for preparing electrodes. Torsion balances of the Milligram Balance type, with ranges of 0 to 50 mg and 0 to 250 mg, have been employed. The balances were fitted with dish-shaped polished aluminum pans, in which a funnel-like hole was made to permit rapid transfer of powdered charges to the electrode. Tapping the side of the pan is sufficient to cause the powder to slide smoothly and completely through the hole

into an electrode. The use of metal pans avoids the difficulty encountered with static electric charges when glass weighing dishes are employed. The anode caps for the electrodes, figure 5, are prepared from high-purity graphite rods on a cutter similar to that made by the ARL-Dietert Co., but provided with a drilling tool at each end of the motor shaft, one tool for drilling the sample cup and the other for drilling the tapered mounting cup. The dimensions of the drills and other tools are shown in figure 6. The cathodes are sharpened to a point in a pencil sharpener fitted with a stainless-steel guide sleeve. The anode pedestal is readily prepared by placing the tip of a cathode electrode piece through the hole in the pedestal-forming tool (fig. 6) and then removing the protruding tip. The anode cap, *A*, is employed throughout the carrier-distillation procedure. Anode cap, *B*, is employed in a procedure involving complete burning of the sample, which, in the case of uranium oxide samples, is applied only for the determination of calcium (see note under section III, 2 (e)).

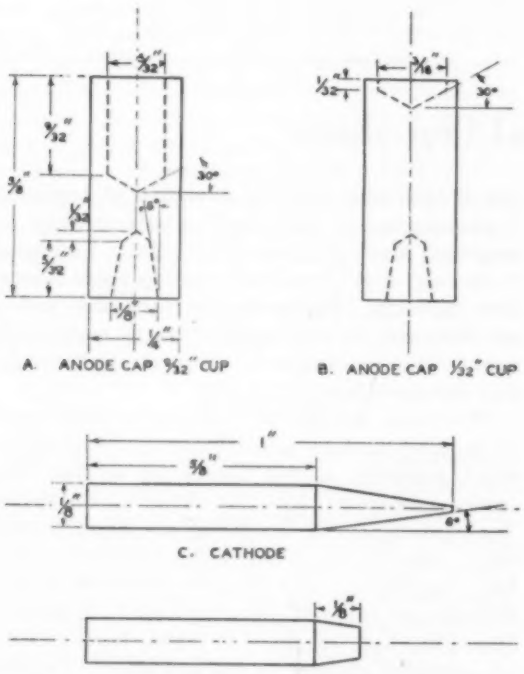

FIGURE 5.—*Electrode shapes.*

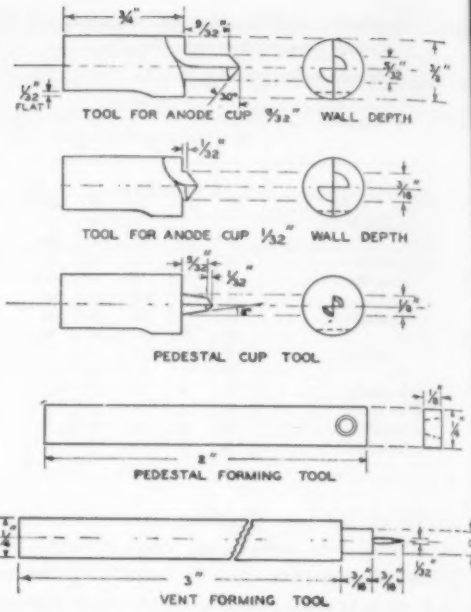
TOOL FOR ANODE CUP 9/32" WALL DEPTH
TOOL FOR ANODE CUP 1/32" WALL DEPTH
PEDESTAL CUP TOOL
PEDESTAL FORMING TOOL
VENT FORMING TOOL

FIGURE 6.—*Tools employed in preparing electrodes.*

2. Analysis of Uranium-Base Material

(a) Preparation of the Sample

Samples of uranium-base materials not in the form of the black oxide U_3O_8 are converted to this refractory form prior to analysis. Procedures for the conversions were established in the Bureau's chemistry division by C. J. Rodden and others, as follows. Uranium metal in pellet form and various oxides may be ignited in a furnace at 800° to 900° C in quartz dishes for 2 or 3 hours or overnight. Powdered uranium metal is highly pyrophoric and should be ignited cautiously by warming small amounts in a quartz dish in the open. Salts such as the acetate and nitrate may be converted in platinum dishes, beginning at 350° C, stirring the sample until the compound is decomposed, and then completing the ignition at 800° C. The conversion of halide salts by this procedure may result in losses of volatile impurities as halides. To minimize losses, the salts may be hydrolyzed and the ignition completed as before. Ignition generally results in loss of mercury and, in the case of halides, of boron as well. In certain cases (oxides, tetrafluoride) the original sample is examined for these elements by a carrier-distillation procedure in which the exposure is limited to 15

conds, beginning when the arc is struck. The termination of cadmium in samples in which senic exceeds 50 ppm requires the removal of senic to avoid the interference of the lines 2288.12 A and Cd 2288.02 A. The arsenic may removed from a portion of the sample by treatent with portions of concentrated HBr. The salt finally converted to oxide.

In preparing the black oxide sample for spectroaphic analysis, a 4- or 5-g portion is ground for minutes to eliminate segregation. Then a rtion of 200 to 1,500 mg, depending on the mber of runs to be made, is ground with the rrier in the proportion of 98 parts U_3O_8 to 2 parts a_2O_3. A charge of 100 mg of the mixture is nsferred to a graphite anode having a $\frac{5}{32}$-in. up. Similar electrodes are prepared for the mple in duplicate and for selected check standrds. Prior to making the exposures, the charge provided with a vertical vent hole, employing e vent-forming tool shown in figure 6. In neral, eight exposures, including two or three tandards are made on a 4- by 10-inch photoaphic plate; each exposure represents five steps the step sector, with a total spectral-line length 10 mm. The large number of elements deterined and the sensitivities required, involves the bservation of spectra in several regions of pectrum, as described in the following sections.

(b) General Procedure: Determination of 26 Elements

This procedure provides for the determination of s many elements as possible on a single 4- by 0-inch spectrogram in the ultraviolet region of the pectrum. The remaining procedures c, d, e, and are modifications of the general procedure for he purposes of (1) increasing the accuracy or the ensitivity in certain cases, and (2) observing lements not having their most sensitive lines in he general region. The elements determined in he general procedure include iron, magnesium, nd manganese, which are determined with highest ccuracy in procedure (c), and sodium, which is bserved in procedure (e) when the highest sensitivity is required for this element. Boron and silicon re determined by photometric measurement. The conditions and wavelengths employed are given in table 4. The ultimate lines Mg 2852.13, Ni 3414.76, and Sn 3175.04 do not appear in the list because of the availability of other lines sufficiently sensitive and more conveniently located for observation.

TABLE 4.—*Spectral observations for the general procedure*

Determination by visual inspection: Ag, Al, As, Au, Be, Bi, Co, Cr, Cu, Fe, Ge, In, Mg, Mn, Mo, (Na), Ni, P, Pb, Sb, Sn, Tl, V, Zn.

Determination by photometric measurement: B, Si.

Region: 2200 to 3500 *A*, First order 5.6 *A* per mm.

Plate: Eastman Spectrum Analysis No. 1.

Pre-arc period: 5 seconds.

Exposure period: 35 seconds.

Element	Wavelength	Sensitivity [a]	Element	Wavelength	Sensitivity [a]
	A	*ppm*		*A*	*ppm*
Ag	3280.68	0.05	Mg	2776.69	
	3382.89			2778.29	
Al	3082.16	5		2779.83	
	3092.71			2781.42	
As	2349.84	5		2782.97	
	2780.20			2795.53	.5
Au	2427.95			2802.70	
	2675.95	.3	Mn	2794.82	1
B	[b]2496.78			2798.27	
	2497.73	.08		2801.06	
	2348.61	.1	Mo	3132.59	1
Be	3130.42			3170.35	
	3131.07			3193.97	
Bi	2897.98		Na	3302.32	150
	3067.72	.5		3302.99	
Co	2424.93		Ni	3002.49	2
	3453.50	1		3050.82	
	2762.59		P	2553.28	50
Cr	2835.63			2554.93	
	2843.25	3	Pb	2802.00	1
	3247.54	.3		2833.07	
Cu	3273.96		Sb	2598.06	10
	2599.40			2877.92	
	2788.10		Si	[b]2506.90	
Fe	3020.64	1		2514.33	
	3021.07			2516.12	
	2651.18	.2		2881.58	3
Ge	2651.58		Sn	2863.33	
	2754.59			3262.33	1
In	3039.36		Tl	2767.87	3
	3256.09	.5	V	3183.41	
				3183.98	5
				3185.40	
			Zn	3282.33	
				3345.02	20

[a] The limit of detection is indicated for the line of greatest sensitivity.

[b] These lines are employed for photometric measurement in this procedure.

(c) Improved Determination of Fe, Mg, and Mn

This procedure is identical with that of procedure (b), except that the carrier contains chromium, added as an internal standard for the determination of iron, magnesium, and manganese by photometric measurement. The carrier is composed of Ga_2O_3 containing 1 percent of chromium as Cr_2O_3. The wavelengths employed are given in table 5.

TABLE 5.—*Analytical line pairs for the determination of* Fe, Mg, *and* Mn

Wavelengths, A	Index value [a]
	ppm
Fe II, 2599.40/Cr II, 2762.59	63
Mg II, 2802.70/Cr II, 2843.25	12
Mn I, 2798.27/Cr. II, 2843.25	40

[a] The index value in the table is the concentration of the element for which the intensity ratio of the pair of lines is unity.

(d) Determination of Cd and Hg

This procedure is designed for the determination of cadmium at maximum sensitivity by photographing the line Cd 2288.02 A with the increased dispersion of the second order of the grating. Interference by the line As 2288.12 A will be encountered when arsenic exceeds a concentration of 50 ppm and, in this case, a sample treated for removal of arsenic should be employed. The procedure provides the proper observing conditions for the determination of highly volatile mercury in samples that have not been ignited. The observing conditions and wavelengths employed are given in table 6.

TABLE 6.—*Spectral observations for* Cd *and* Hg

Wavelength region: 2200 to 2935 A, second order 2.8 A per mm.
Plate: Eastman Spectrum Analysis No. 1.
Pre-arc period: None.
Exposure period: 25 seconds.
Wavelengths employed and remarks:
Cd 2288.02, sensitivity 0.07 ppm, is measured photometrically. Caution: If As 2349.84 is present, As 2288.12 may interfere with the Cd line, but is resolved at concentrations below 50 ppm.
Hg 2536.52, sensitivity 10 ppm.

(e) Determination of Ba, Li, and Na

This procedure provides for highest sensitivity in the determination of lithium and sodium by photographing the spectrum in the visible region. The region is convenient also for the determination of barium.[4] An analytical curve was established for the photometric measurement of Li 6707.84 A, but lithium is seldom detected and measurements are not regularly made. The conditions employed are given in table 7.

[4] Calcium is determined by a complete-burn procedure employing a shallow cup electrode with a charge of 5 mg of the sample mixture prepared for the carrier-distillation method. A 10-ampere arc is employed, and the spectrum is photographed in the region of the calcium line 3933.67 A with an Eastman Spectrum Analysis No. 1 plate. The sensitivity of detection for calcium is 2 ppm. A procedure for the determination of strontium was not established.

TABLE 7.—*Spectral observations for Ba, Li and Na*

Wavelength region: 5700 to 7000 A, first order 5.5 A per mm.
Plate: Eastman Spectroscopic II-F.
Pre-arc period: None.
Exposure period: 40 seconds.

Wavelength	Sensitivity
A	*ppm*
Ba, 6141.72	10
Li, 6707.84	0.1
Na 5889.95	.5
Na 5895.92	

(f) Determination of Cs, K, and Rb

This procedure is identical with that of procedure (e) except that the spectrum is photographed in the infrared region for high sensitivity of detection of cesium, potassium, and rubidium. The conditions employed are given in table 8.

TABLE 8.—*Spectral observations for* Cs, K, *and* Rb

Wavelength region: 7450 to 8750 A, first order 5.5 A per mm.
Plate: Eastman Spectroscopic I-N.
Pre-arc period: None.
Exposure period: 40 seconds.

Wavelengths	Sensitivity
A	*ppm*
Cs, 8521.10	8
K 7664.91	2
K 7698.98	—
Rb, 7800.23	1

IV. Summary

A method of fractional distillation for spectrographic analysis is described for the separation of volatile impurities from a refractory sample matrix. The separation is obtained by the addition of a small amount of a selected volatile carrier material to the refractory sample, followed by partial distillation of the mixture in a d-c arc electrode assembly of improved design. The functions of the carrier (1) to sweep out the minute quantities of impurity vapors, and (2) to stabilize the arc, result in high sensitivity and accuracy for the determination of 33 impurity elements at concentrations of a few parts per million or less in uranium-base materials. The accuracy observed for determinations of B, Cd, Fe, Mg, Mn, and Si, by photometric measurement, was ±10 percent. The method was applied to control and inspection in the production of high-purity uranium metal, oxides, and salts within the Manhattan Project.

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Vacuum-Tube Acceleration Pickup

By Walter Ramberg

The vacuum-tube acceleration pickup consists of a fixed indirectly heated cathode and two plates on either side of the cathode which are mounted elastically to deflect in response to acceleration normal to the plane of the plates. The tube has a natural frequency of about 800 cycles per second, and it has a flat response for sinusoidal accelerations from 0 to 200 cycles per second with enough output at accelerations of the order of 10 g to drive a recording galvanometer directly without the complications of an amplifier. The use of the tube is recommended in those applications in which its peculiar advantages of high natural frequency, ability to withstand large accelerations, and linearity outweigh the disadvantages of zero drift, warming-up time, high current consumption, and the need of filtering to remove natural frequency response.

I. Introduction

The vacuum-tube acceleration pickup described in this paper represents the most recent stage in a development which has been carried on for the Bureau of Aeronautics, Navy Department, at the National Bureau of Standards and at Sylvania Electric Products, Inc., since 1941.

The purpose of the investigation was to develop an acceleration pickup that would have a flat response for sinusoidal accelerations with frequencies up to 300 c/s and that would have enough output at accelerations of the order of 10 g to drive a recording galvanometer directly without the complication of an amplifier. It was thought from the beginning that this might be accomplished with a vacuum tube in which acceleration causes electrodes to deflect elastically relative to each other.

The relative deflection of electrodes in a vacuum tube had been used as early as 1936 by Ross Gunn of the Naval Research Laboratory [1] for measuring small displacements. A more recent application is the microphonic electron tube for measuring small changes in pressure, which was proposed by Jerome Rothstein in 1943.[2]

[1] Ross Gunn, Apparatus for the detection of displacements, U. S. Patent 2,155,620. Reissued Feb. 27, 1940, Re. 21,372.

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II. Characteristics

1. Construction

The vacuum-tube acceleration pickup is a twin diode consisting of a fixed indirectly-heated cathode and two plates, one to either side of the cathode. The plates are elastically mounted to deflect in response to acceleration normal to the plane of the plates.

Figure 1 shows the arrangement and mounting of electrodes in a vacuum tube of a type of which an experimental lot of 95 was built by Sylvania Electric Products, Inc. as type SD 759. The cathode, C, is anchored in the two mica plates, M. The mica plates, M, are connected into a rigid box by transverse bars B_1, B_2, B_3, B_4. The box is fastened to the base of the tube by vertical pins, B_5, B_6, B_7, B_8. The two anode plates, P_1, P_2, consist of thin sheet metal wrapped into a closed rectangular section; this reduces the mass of the plates to a low value, thereby reducing the warming-up time of the electrodes. The plates are connected to two relatively slender vertical rods, R_1, R_2, and R_3, R_4, respectively. These rods are welded to transverse bars B_3, B_4. The plate leads are brought from the transverse bars B_3, B_4, to the vertical pins, B_9, B_{10}, B_{11}, B_{12}, by two heavy connectors each.

The fundamental frequency of the plate structure for bending normal to the plane of the plate was computed by treating the structure as an elastic system with a concentrated mass at the center of gravity of the plate and distributed masses in the supporting wires, which are subjected to flexure and torsion by the vibration of the plate normal to its plane. The diameters and lengths of the wires were computed to give a fundamental frequency in this mode of vibration of the order of 750 c/s. The natural frequencies of vibration in other modes were estimated to be much higher than 750 c/s.

Figure 1 (c) shows the complete pickup. It is housed in a T–9 glass envelope approximately 2 inches long and has a loctal base.

2. Frequency

The lowest natural frequency was determined experimentally by connecting the pickup into the Wheatstone bridge circuit of figure 2 with a cathode-ray oscilloscope between C and D, tapping the pickup with a pencil or a finger, and matching the output on the oscilloscope by the output of known frequency for an audio oscillator.

The natural frequency for the 95 pickups of this design that have been built was found to

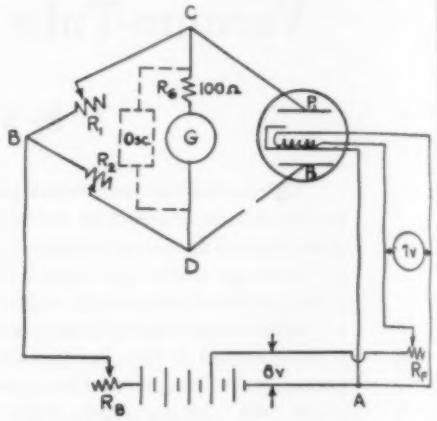

FIGURE 2.—*Wheatstone-bridge circuit for measuring and recording output of tube.*

between 595 and 915 c/s, with an average value of 847 c/s.

3. Resistance

The resistances R_{P1}, R_{P2} from each plate to the cathode were measured with the Wheatstone bridge of figure 2 after a warming-up time of several minutes. The heater voltage was taken as 7 volts and the plate voltage as 10 volts. These are the normal operating voltages for which the tube had been designed. The bridge was balanced by adjusting R_B, R_1, R_2 until the potential difference between A and B, as measured with a voltmeter, was 20 volts, and that between A and C, and A and D was 10 volts. Under this condition of balance, R_1, R_2 must be equal to R_{P1}, R_{P2}, respectively.

The resistances R_{P1}, R_{P2} for the 95 tubes ranged from 88 to 314 ohms, with an average value of 157 ohms. The ratio of the larger one of the two resistances to the smaller one was from 1.0 to 1.46, with an average value of 1.15.

The resistance of the heater at 7 volts was of the order of 14 ohms. The total power consumption in the circuit of figure 2 is, therefore, of the order of 7 watts.

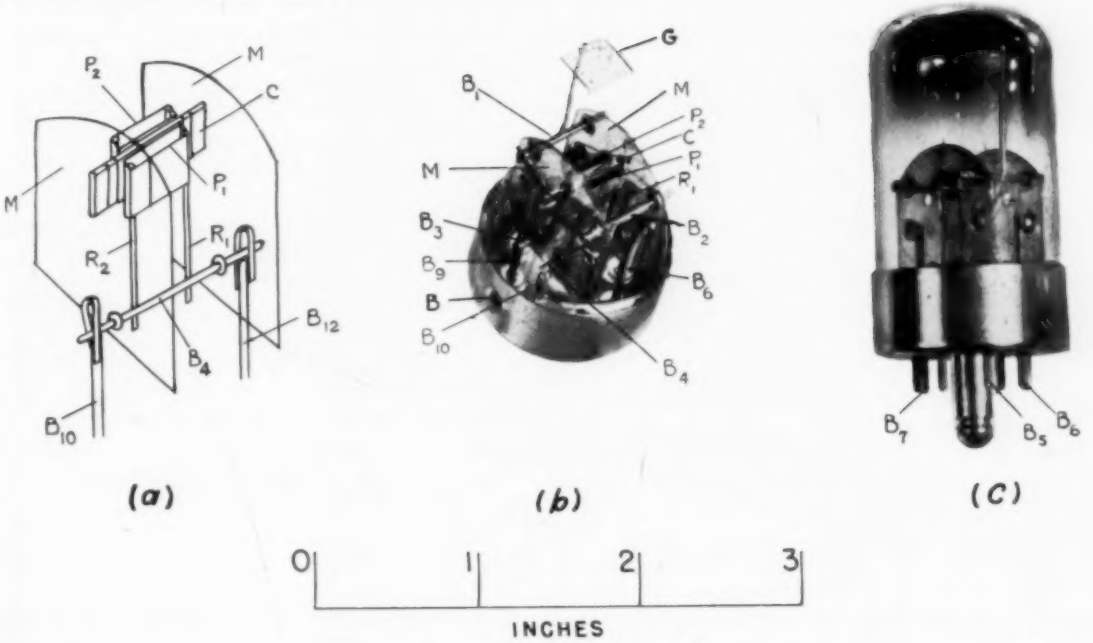

FIGURE 1.—*Arrangement of electrodes in tube.*

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4. Calibration Factor

The calibration factor was computed from the output corresponding to a change in acceleration $2g$ on the assumption of direct proportionality between acceleration and relative change in plate-cathode resistance. This assumption has been verified experimentally for accelerations up to $45g$. The tube was connected into the Wheatstone-bridge circuit, figure 2, which was roughly balanced by making the resistances R_1, R_2 equal to the previously measured plate-cathode resistances R_{P1}, R_{P2}. The resistances R_1, R_2 were adjusted further, keeping their sum constant until the pointer on galvanometer G was near the middle of the scale. The tube was allowed to warm up for 15 minutes, and was then slowly rotated with its axis horizontal through 360 degrees, and the maximum and minimum currents were noted on a galvanometer, G, with an impedance of 100 ohms between C and D. The maximum unbalance current corresponded to $+1g$ on one plate (in a horizontal position on top) and the minimum current corresponded to $-1g$ on the same plate (in a horizontal position on the bottom). The difference in unbalance current I_{2g} therefore corresponded to a change in acceleration $2g$. The calibration factor, K, was computed from the following equation, derived in the appendix:

$$K=\frac{\Delta R}{R}\Big/\frac{a}{g}=\left(5+\frac{R_{P1}+R_{P2}}{40}\right)I_{2g}, \qquad (1)$$

where $\frac{\Delta R}{R}=\frac{1}{2}\left(\frac{\Delta R_{P1}}{R_{P1}}+\frac{\Delta R_{P2}}{R_{P2}}\right)$=average relative change in plate-cathode resistance corresponding to acceleration, a, normal to the plate.

The values of K for the 95 tubes ranged from 0.0029 to 0.0072, with an average value $K=0.0045$. This corresponds to an output of the order of 0.2 ma/g. The sensitivity of the tube, as measured by the calibration factor K, depends on the plate voltage and on the heater voltage. Tests have indicated that K may be increased about 40 percent by increasing the plate voltage from 10 to 12 volts, keeping the heater voltage at a constant value between 6.5 and 7.0 volts.

5. Response to Transverse Acceleration

The response to transverse acceleration was measured on a shaking table vibrating sinusoidally at 32 c/s. with a displacement amplitude of about 0.05 inch, producing an acceleration amplitude of about $5g$. The tube was first placed with the acceleration normal to the plates and then with the acceleration parallel to the plates and normal to the axis of the tube. The transverse response was measured by the ratio of amplitudes on a cathode-ray oscilloscope, with the tube in the second and in the first position.

The transverse response was found to be negligible for the first batch of six tubes that was tested. Tests on the remaining tubes were omitted as superfluous.

6. Wave Form

The wave form was observed on a cathode-ray oscilloscope when the tube was mounted on the end of a cantilever beam, which was vibrated in its fundamental mode as a free elastic body. There was no visible deviation from a sinusoidal shape for each one of the 10 tubes tested for wave form.

7. Stability

The zero drift was measured by connecting the tube into the Wheatstone-bridge circuit of figure 2 and recording the change in unbalance current with time without subjecting the tube to any change in acceleration. The measured change in unbalance current was divided by the change in current $I_{2g}/2$, corresponding to an acceleration of $1g$, in order to express the drift as a "drift in g."

The zero drift in 15 minutes, after a warming-up period of 15 minutes, exceeded $1g$ for 30 of the 95 tubes; it was less than $0.2g$ for 25 tubes; it was too small to be measured for 7 tubes.

Large drifts could be traced sometimes to temperature changes around the tube, to fluctuations in heater voltage, or to poor electric contact in the connections to the base of the tube. The drift could be reduced in such cases by enclosing the tube in a small box, by controlling the heater voltage, or by soldering the leads from the bridge to the pins projecting from the base of the tube. However, an unpredictable drift of the order of $\pm 1g$ in a few minutes took place from time to time in certain tubes, even after all these precautions were taken. Fortunately, the drift tends to decrease with the age of the tube. Twenty-nine tubes that showed drifts in excess of $1g$ were

retested after 6 months of storage. Of these tubes, none had drifts exceeding 1g, 12 had drifts from 0.2g to 1.0g, and 17 had drifts below 0.2g.

Some measurements of zero drift were made at a plate voltage of 12 volts and a heater voltage of 6.5 volts, which, as mentioned above, may lead to an appreciable increase in sensitivity. The drift at these voltages was either less than or equal to that measured at the voltages spcified in figure 2.

8. Range of Linear Response

The tubes were originally designed for a maximum acceleration of 20g. However, experience has indicated that they will function under much higher accelerations.

One tube was calibrated at accelerations up to 45g by attaching the tube to a shaking table, which was run at constant amplitude of about 0.19 inch up to a speed of about 50 c/s. The tube was connected into the Wheatstone bridge of figure 2, and the unbalance current of the bridge was fed into a type C galvanometer (internal resistance, 9 ohms; frequency, 430 c/s; d-c sensitivity, 2 mm/ma) in a Heiland six-channel oscillograph. The unbalance current was recorded as the shaking table was allowed to coast down after switching off the current to the driving motor. It was found that the unbalance current was a linear function of the acceleration over the whole range of the measurements. At a later date the same tube was subjected to an acceleration of 117g on the same shaking table; its output was found to correspond to the same calibration factor as that obtained on the calibration to 45g.

Other tubes were frequently subjected to accelerations well above 20g without showing a change in calibration factor. However, severe and prolonged shaking was in several instances accompanied by a shift in the "zero."

III. Method of Using Pick-up

The method of using the vacuum-tube acceleration pickup is most readily illustrated with a specific example.

Figure 3 shows a tube in use for recording vertical accelerations at the center section of a model "airplane" subjected to a drop test.

The tube is connected into the Wheatstone bridge of figure 2, which is built into the control panel of figure 4. This control panel is equipped with a meter, M, which may be switched in to indicate heater voltage, plate voltage, or unbalance current.

Connections to the pins projecting from the base of the tube were made by soldering on leads of No. 24 insulated copper wire. The soldering was done carefully to avoid damage to the glass seal around the pins by overheating. Solder connections were used in preference to connections through a standard socket to eliminate errors from changes in contact resistance between pins and sleeves in the socket. Parallel pairs of wires were used in each heater lead to prevent excessive heating and to retain the flexibility of the No. 24 wire.

Special care was taken to clamp the tube to the structure in such a manner that it would experience the same acceleration as the structure. For this purpose the tube was clamped at the metal sleeve in a split clamp of $\frac{1}{32}$-inch brass tubing, which is shown in figure 5. A layer of transparent scotch tape was wrapped on the metal sleeve of the tube before inserting in the clamp to distribute the clamping force, thereby preventing breakage of the glass envelope during clamping.

The tube was then allowed to heat up at least 15 minutes to attain equilibrium. A type G galvanometer in a Heiland six-channel oscillograph was connected in at G in figure 2 with suitable resistance in series or in parallel to limit the sensitivity to a safe value. The resistor R_1 was adjusted while gradually increasing the sensitivity until the galvanometer indicated balance. The resistor R_F in the heater circuit was then adjusted until the meter, M, in the control panel, figure 4, indicated 7 volts. The resistor R_B in series with the bridge was next adjusted until the meter indicated 10 volts.

The balance of the bridge was again checked and, if necessary, adjusted.

The recorded output of the tube was calibrated by subjecting the tube to a change in acceleration 2g and recording the change in output. For this purpose the plates were first placed horizontally with button B, figure 1, at "9 o'clock" and the output was recorded. Then the tube was rotated about its horizontal axis to place the button at "3 o'clock" and the output was recorded again.

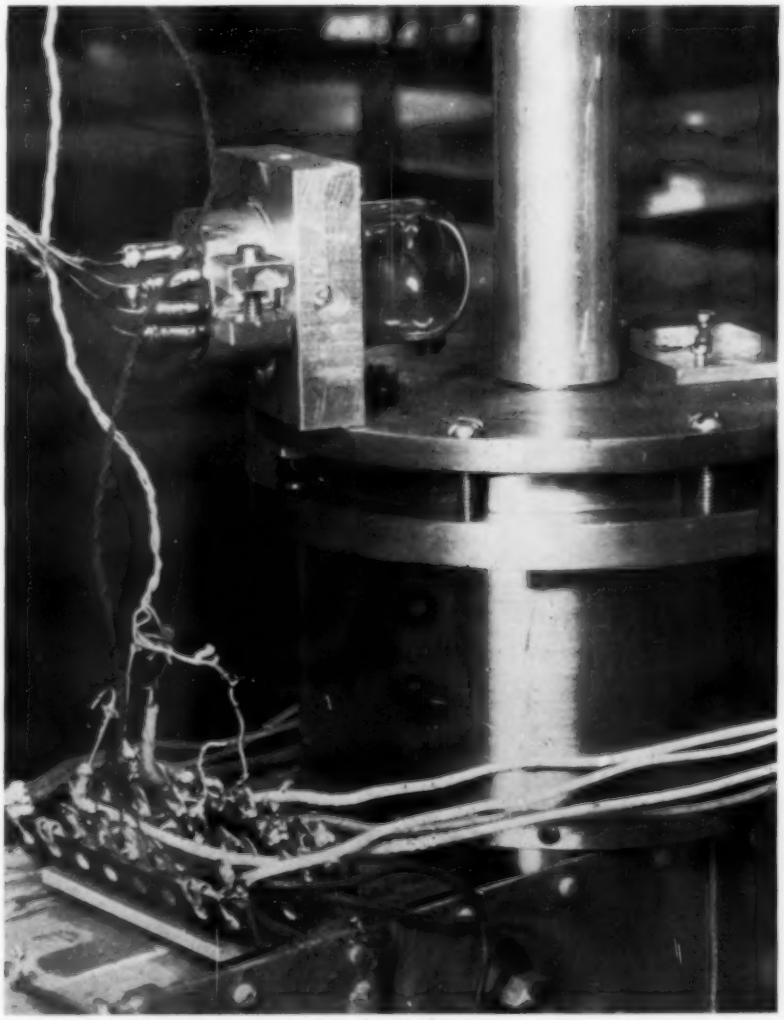

FIGURE 3.—*Tube mounted for recording vertical acceleration at center section of model "airplane".*

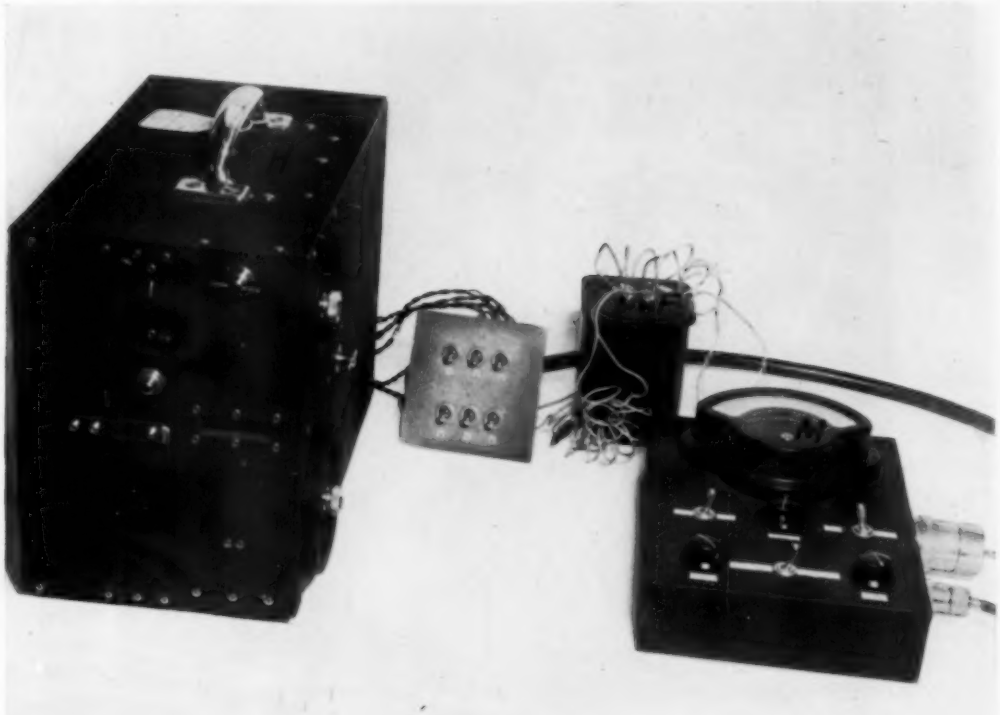

FIGURE 4.—*Recorder, filter, and control panel for tube.*

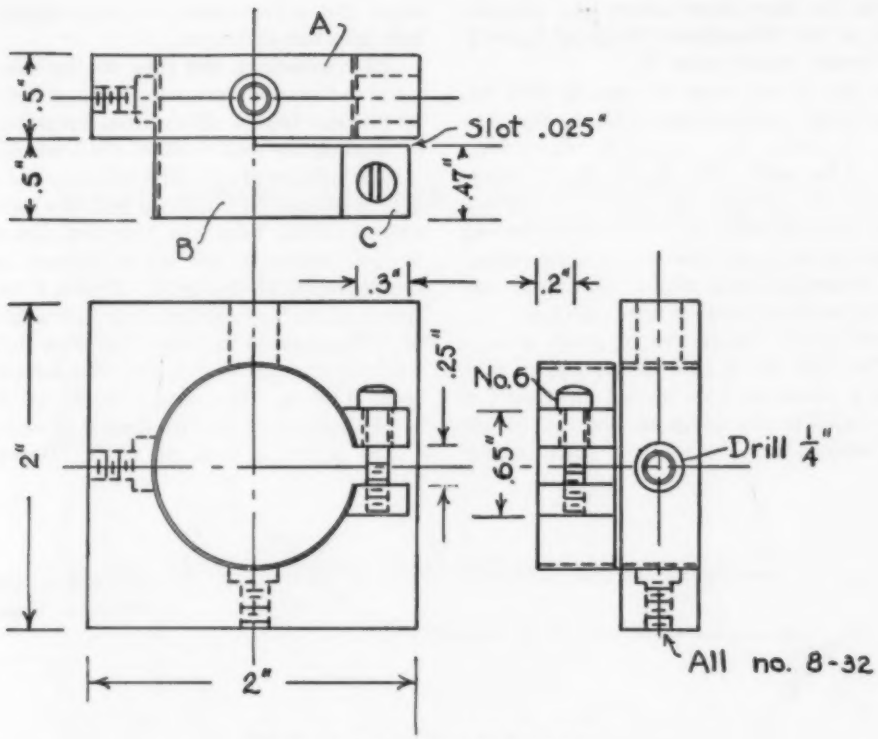

FIGURE 5.—*Split clamp for holding tube.*

A, Aluminum alloy; *B*, 1¼-in. by ⅛-in. brass tube, press fit in *A*; *C*, brass lugs, silver solder to *B*.

Rotation through 180 degrees is particularly simple when the tube is held in the square-edge clamp of figure 5. Rotation with the clamp has the additional important advantage of preventing errors in indicated output caused by changes in physical contact between the tube and its surroundings.

In some applications in which the accelerations to be recorded are much larger than $2g$, it is necessary to calibrate with a larger output on the recording paper.

The larger output may be obtained either directly by imposing larger accelerations or indirectly by increasing the sensitivity (lowering the attenuation) for the calibration at $2g$ by a known factor.

A portable calibrator has been developed at the National Bureau of Standards for applying known accelerations up to $20g$ to four vacuum-tube acceleration pickups simultaneously.

Figure 6 shows a simple circuit for changing the sensitivity, or attenuation, by a factor α with-

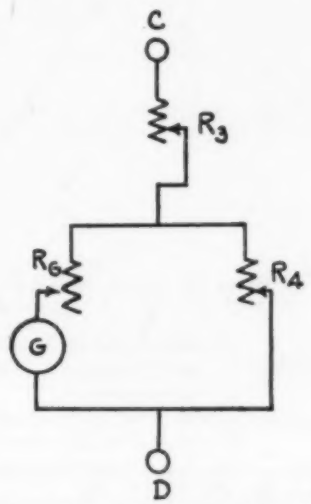

FIGURE 6.—*Circuit for changing sensitivity of tube without changing input impedance into recorder.*

α=attenuation; $R_3=(1-\alpha)\,R_\theta$; $R_4=\frac{\alpha}{1-\alpha}R_\theta$.

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out changing the impedance across the balance points C, D, of the Wheatstone bridge of figure 2 from a previously chosen value R_G.

For example, if we want to record with an attenuation $\alpha=0.1$ and calibrate with an attenuation $\alpha=1$, we have for recording, $R_3=0.9R_g$, $R_4=R_G/9$; and for calibrating, $R_3=0$, $R_4=\infty$ (open circuit).

After the tube was calibrated, it was attached to the structure at the point for which acceleration was to be recorded, with plates normal to the component of acceleration that was to be recorded. The clamp was fastened to the structure with a screw passing through a hole in the clamp and fitting into a threaded hole in the structure; a recess is provided in the clamp for the head of the screw. A C-clamp may be used in place of the screw if it is inadvisable or inconvenient to drill a hole into the structure.

After attaching the tube to the structure, the leads to the tube were collected and fastened down to prevent failure either from breaking the lead or bending the pins to which the leads are soldered.

The balance of the tube was checked once more before the test. The drop test was made and the output of the tube was recorded directly with a type C galvanometer on a Heiland six-channel oscillograph, H, figure 4. Figure 7 (a) shows a record of such a drop test, together with the record of calibrations at $2g$ before and after the test. The model is dropped at A and the acceleration changes from g to 0. The model lands at B and the acceleration rises rapidly from 0 to about $4g$ at C.

The record is clear up to D. Beyond D it is

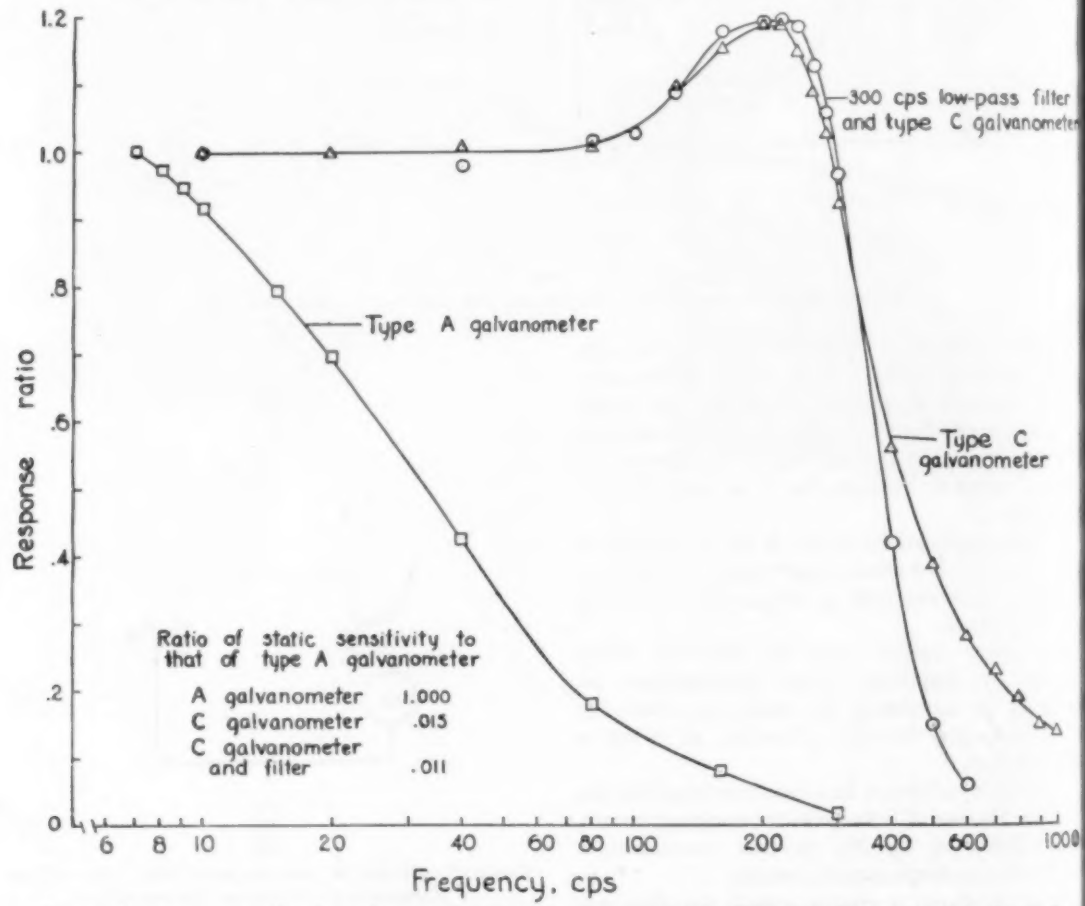

FIGURE 8.—*Response ratios for galvanometers and filter when used with Wheatstone-bridge circuit in figure 2.*

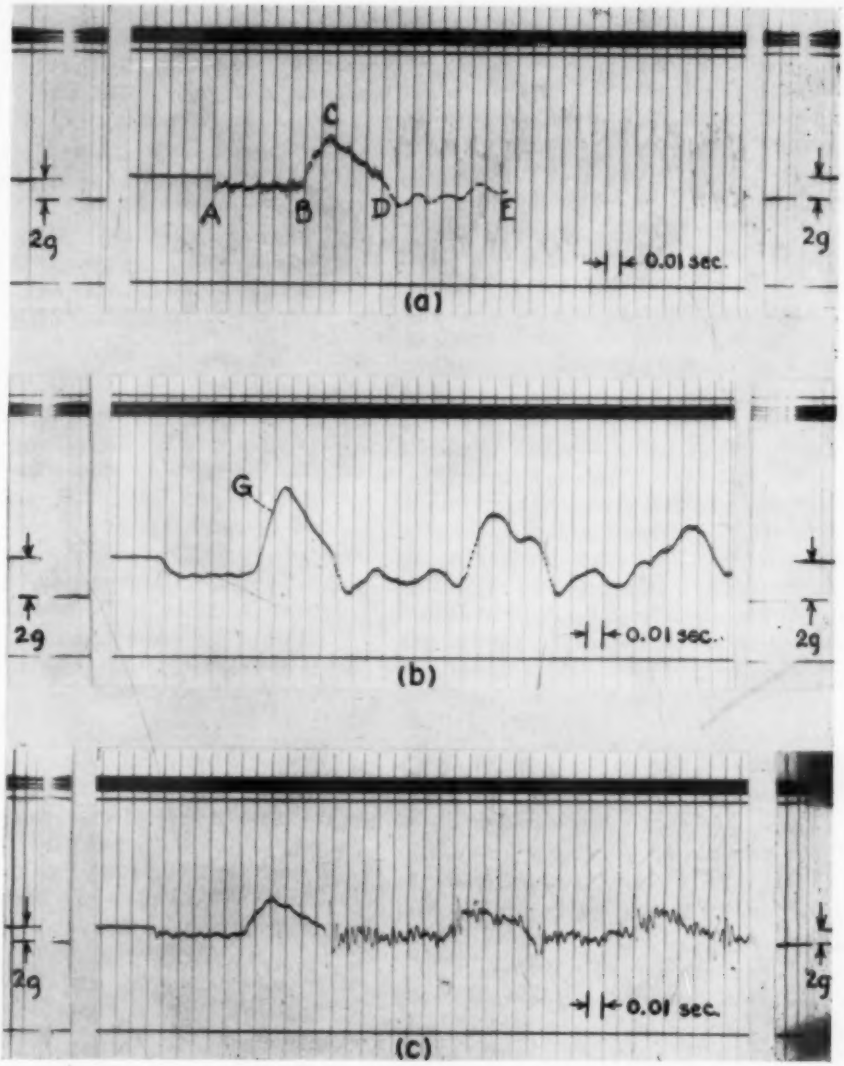

FIGURE 7.—*Records of identical drop tests with high-frequency galvanometer type C without filter, low-frequency galvanometer type A without filter, and high-frequency galvanometer type C with filter.*

(a) Type C, no filter; (b) type A, no filter; (c) type C, UTC filter.

rred by superimposed oscillations at the natural quency of the plates in the tube (about 800 c/s), ich are too faint to be clearly seen in figure 7 . The acceleration can be estimated, never-less, as long as the superimposed oscillation is rly recorded, by connecting the mean points of oscillation. This is indicated by the dotted ve in figure 7 (a). But even this expedient ls beyond E, where the oscillations become of large amplitude to be recorded.

Satisfactory records can be obtained under se conditions by reducing the recorded output the natural frequency of the tube. This may accomplished either by using a recording gal-nometer, which is more efficient in attenuating rations at the natural frequency of the tube, or inserting a suitable electric filter.

The response ratio (ratio of sensitivity to d-c sitivity) of the type C galvanometer at the ural frequency of the tube (800 c/s) is about 9 according to figure 8; this is apparently ufficient to reduce natural frequency response an acceptable value.

Figure 7 (b) shows a record obtained with a land type A galvanometer which has a natural quency of 40 c/s as compared to 430 c/s for the e C galvanometer. The response ratio at c/s is less than 0.01, according to figure 8. e output of the tube was attenuated to 0.029 of its former value in order to compensate for the increased sensitivity of the type A galvanometer as compared to the type C galvanometer. The record is much easier to follow than that of figure 7 (a); however, it is unsatisfactory insofar as the galvanometer is unable to follow rapidly varying accelerations, as at G, because of its relatively low natural frequency.

A satisfactory record without appreciable response at the natural frequency may be obtained by inserting a low-pass filter, F, figure 4, between the bridge and the galvanometer. Figure 8 shows the response curve for a type C galvanometer with a filter (UTC filter 93051) built by the United Transformer Co., which has proved satisfactory for this purpose. This filter is practically flat up to 300 c/s and cuts off sharply to a relative response of less than 0.01 at 800 c/s. The weight of the filter is less than 3 pounds.

Figure 7 (c) shows a record of the drop test with the filter placed ahead of the galvanometer, as shown in figure 4. The record gives the same accelerations as figure 7 (a) and the response at the natural frequency has been suppressed. The vibrations with a frequency of about 250 c/s in the right-hand portion of the record were ascribed to elastic oscillations of a portion of the model "airplane" excited by the rebound from the landing impact. Insertion of the filter has resulted in a loss of current sensitivity of about 30 percent.

IV. Field of Application

The use of the vacuum tube is recommended in se applications in which its peculiar advantages igh output, high natural frequency, high capac- and linearity outweigh the disadvantages of drift, warming-up time, high-power consump-n (about 7 watts for tube and Wheatstone dge of fig. 2), and the need of filtering to remove ural frequency response.

potential advantage of the vacuum tube eleration pickup over other acceleration pick-s is the possibility of building it at relatively cost in large quantities using the special nics developed by the manufacturers of uum tubes.

he high output and high natural frequency of vacuum tube makes it possible to record dly varying accelerations without requiring amplifier. This is a desirable feature in flight of small airplanes where space and weight are at a premium. It also simplifies tests in the laboratory when amplifying channels are not readily available.

The high capacity of the pickup is advantageous in recording accelerations over a wide range and in preventing damage from sudden high accelerations.

The linearity of the pickup makes possible the filtering out of high-frequency response, regardless of amplitude to produce a record proportional to acceleration.

The zero drift found in most of the tubes makes them unsuitable in those flight tests in which the imposed acceleration is unknown over periods of time measured in minutes. The zero drift is not serious in recording either very large accelerations or in recording changes in acceleration over a period of time measured in seconds. Typical

illustrations of the latter are drop tests, and impact tests in which the impact is softened by cushioning, so that it can be recorded with a pickup having a flat response up to 300 c/s.

The warming-up time of 15 minutes represents a drain on the available power, which may be serious in certain applications. It also introduces an undesirable delay in adjusting the equipment.

The filter represents an added item of expense (about $40.00) and of weight (about 3 lb), which may be avoided by using pickups of other type with internal damping.

The vacuum-tube acceleration pickup is being tried out under various service conditions by several flight research laboratories to indicate its field of usefulness more specifically. Service experience may also indicate certain improvements in design and construction that would overcome some of the disadvantages of using a vacuum tube to measure accelerations.

V. Conclusion

The vacuum tube acceleration pickup appears to be a convenient means for measuring accelerations in the range from 5g to 40g. It has an advantage over other acceleration pickups in combining high sensitivity with high natural frequency thereby making it possible to record rapidly varying accelerations directly without the complication of an intermediate amplifier. It has a disadvantage over other pickups in being more subject to zero drift, in requiring a warming-up time of about 15 minutes to reach equilibrium, and in requiring a filter to remove response at its natural frequency.

Further experience in the use of the vacuum tube acceleration pickup in flight tests as well as in the laboratory will be necessary to indicate its full scope of usefulness.

The author takes this opportunity to thank the Bureau of Aeronautics for permission to publish this material. He also acknowledges his debt to the engineers of Sylvania Electric Products, Inc., for their cooperation in overcoming many difficult problems in vacuum-tube technic. Finally, he owes a great deal to the constant cooperation of his associates, particularly Wm. R. Campbell, Samuel Levy, and A. E. McPherson.

VI. Appendix

1. Derivation of equation 1

The proof of equation 1 follows from the expression for the current i_G flowing through the galvanometer resistance R_G when the Wheatstone bridge of figure 9 is unbalanced by changing two of the resistances by ΔR_1, $-\Delta R_2$ as indicated. This current, according to page 45 of reference,[3] is:

$$i_G = \frac{E\,[(R_1+\Delta R_1)R_2 - R_1(R_2-\Delta R_2)]}{R_G 2R_1 2R_2 + 2R_1{}^2R_2 + 2R_1R_2{}^2}$$

$$= \frac{E}{4R_G + 2(R_1+R_2)}\left(\frac{\Delta R_1}{R_1} + \frac{\Delta R_2}{R_2}\right). \qquad (2)$$

In our case

$$i_G = I_{2g}$$

$$\left(\frac{\Delta R_1}{R_1} + \frac{\Delta R_2}{R_2}\right) = \left(\frac{\Delta R_{P1}}{R_{P1}} + \frac{\Delta R_{P2}}{R_{P2}}\right) = \frac{2\Delta R}{R}, \qquad (3)$$

where ΔR_{P1}, ΔR_{P2} are the changes in plate-cathode resistance corresponding to a change in acceleration $2g$. Substituting equation 3 in equation 2 and solving for $\Delta R/R$ gives

$$\frac{\Delta R}{R} = (2R_G + R_1 + R_2)\,\frac{I_{2g}}{E}. \qquad (4)$$

In the case of figure 2

$$R_G = 100 \text{ ohms}, \quad E = 20 \text{ volts}. \qquad (5)$$

Inserting equation 5 in equation 4, and remembering the definitions of calibration factor K,[1] gives equation 1:

$$K = \frac{\Delta R}{R}\Big/\frac{a}{g} = \frac{\Delta R}{R}\Big/2 = \left(5 + \frac{R_1+R_2}{40}\right) I_{2g}. \qquad (6)$$

Washington, July 19, 1946.

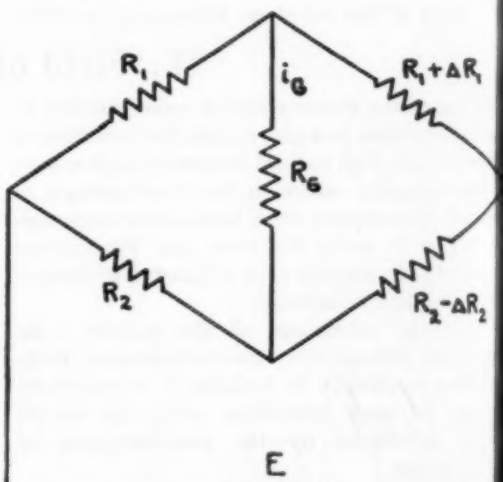

Figure 9.—*Wheatstone bridge with small unbalance in two arms.*

[3] William H. Timbie and Vannevar Bush, Principles of electrical engineering (John Wiley & Sons, Inc., New York, N. Y., 1930).

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Comparative Bond Efficiency of Deformed Concrete Reinforcing Bars

*By Arthur P. Clark**

The purpose of the tests was to determine the resistance to slip in concrete of 17 different designs of deformed reinforcing bars.

The tests were of the pull-out type in which the bars were cast in a horizontal position; the depth of concrete under the bars and the length of embedment were varied. The slip of the bar was measured at the loaded and free ends.

Three tests were made of each variable for each design of deformation.

It was established that a certain group of the bars was definitely superior to the others, in the sense that their average rating was significantly higher than the average of the others. Bars cast in the top position were much less effective than those cast in the bottom position.

I. Introduction

The tests of pull-out specimens reported herein constitute the first phase of a comprehensive investigation on the bond efficiency of deformed concrete reinforcing bars. The investigation was initiated by the Committee on Reinforced Concrete Research of the American Iron and Steel Institute, and was conducted through the medium of a Research Fellowship established at the National Bureau of Standards in Washington.

*Research Associate at the National Bureau of Standards, representing the American Iron & Steel Institute.

II. Materials

1. Reinforcing Bars

The bars, all nominally ⅝ in. in diameter, are illustrated in figures 1 and 2 by two views of each bar to show the pattern of the deformations as produced by the upper and lower rolls and also the relation of the two.

Diameters and areas were determined from the length and weight measurements of the bars. The yield point was determined in a 100,000-lb-capacity testing machine of the beam and poise

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type by observing the drop of the beam. The height of the deformations was measured with a dial gage reading to 1/1000 in. The bar was held in a jig (fig. 3), and readings were taken at three or more points around the bar at each of several positions along the length of the bar. A total of 92 measurements of deformation heights were made by three observers to determine the average heights of the deformations of each bar. The bearing area of the deformations per linear inch of bar was determined from the average height, projected length, and spacing. The two latter dimensions were measured from an impression of the deformations projected on a plane surface made by rolling the bar in a thin layer of quick-setting plaster.

The physical properties of the bars are given in table 1.

TABLE 1.—*Physical properties of deformed reinforcing bars*

Bar No.	Area[1] of bar	Deformations		Yield point	Tensile strength	Elongation, in 8 in.
		Average height	Bearing area			
	*in.*²	*in.*	*in.*²/*in.*	*lb/in.*²	*lb/in.*²	*Percent*
1	0.61	0.045	0.082	44,100	77,700	26.6
2	.58	.046	.149	43,200	74,100	33.6
3	.56	.063	.134	41,000	63,300	34.0
4	.59	.067	.192	37,500	58,900	25.8
5	.65	.040	.322	38,300	70,400	26.7
6	.60	.055	.354	43,900	81,100	21.9
7	.59	.050	.257	45,900	81,100	21.4
8	.61	.055	.390	53,300	77,800	25.4
9	.61	.054	.724	41,100	70,300	25.0
10	.60	.050	.332	43,100	71,000	25.4
11	.61	.027	.101	55,500	98,400	18.7
12	.60	.028	.100	61,000	103,100	19.5
13	.58	.030	.103	63,400	107,100	17.2
14	.59	.067	.102	46,900	81,100	20.3
15	.60	.033	.052	46,100	75,400	25.4
16	.59	.033	.041	35,750	56,000	36.7
17	.60	.....	.....	.....	128,700	11.3

[1] Areas, yield points, and tensile strengths therefrom are based on length and weight measurements in accordance with A.S.T.M. Designation A 15-39. All calculations of stresses in bars in pull-out specimens are based on nominal area (0.60 in.²) of a ¾-in. plain round bar.

2. Concrete

Concrete was machine-mixed and proportioned by weight in the ratio of 1:1.74:2.23. The water-cement ratio was 5.75 gal per sack. Portland cement meeting the current standard specifications of the ASTM for type I cement was used.

The coarse aggregate was Potomac River gravel ranging in size from No. 4 to 1 in. The fine aggregate was Potomac River sand graded as shown in table 2. The dry rodded weight of the gravel was 106 lb/ft³ and the sand 109 lb/ft³.

TABLE 2.—*Sieve analysis of sand*

U. S. Standard Sieve No.	Percentage passing by weight
4	98
8	86
16	71
30	44
50	12
100	3

The slump of the concrete averaged 4¼ in. and the compressive strength of standard 6- by 12-in. cylinders, cured in moist air for 28 days, averaged 5,600 lb/in². The modulus of elasticity at 3 days was 4,140,000 lb/in².

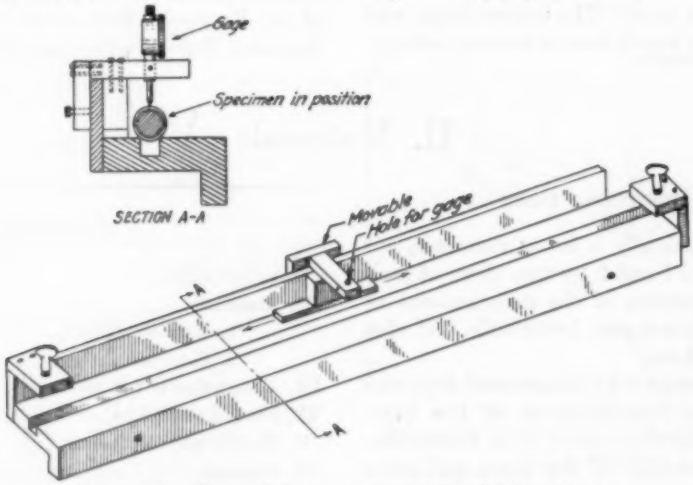

FIGURE 3.—*Jig used in measuring height of deformations.*

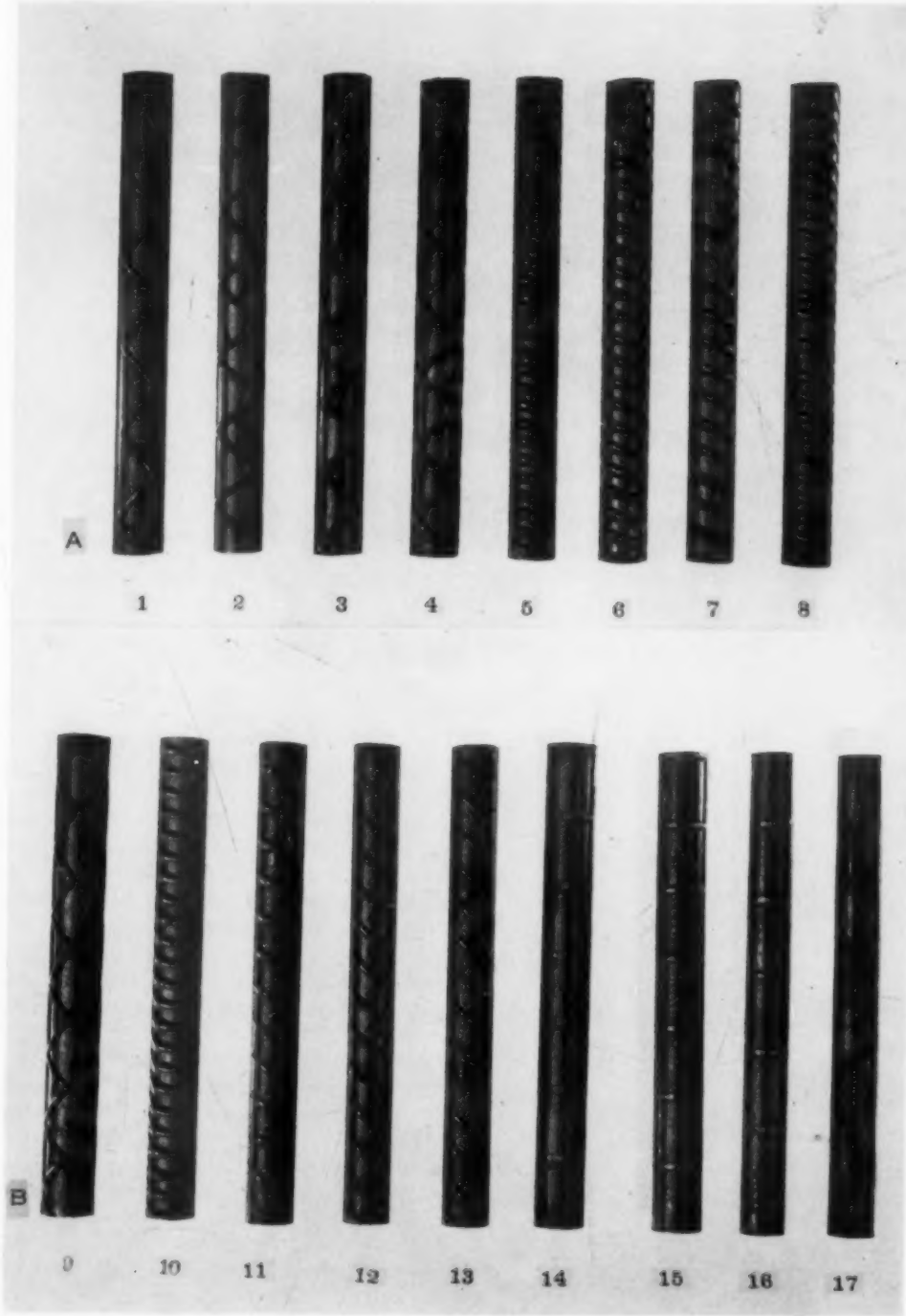

FIGURE 1.—*Types of bars tested.*

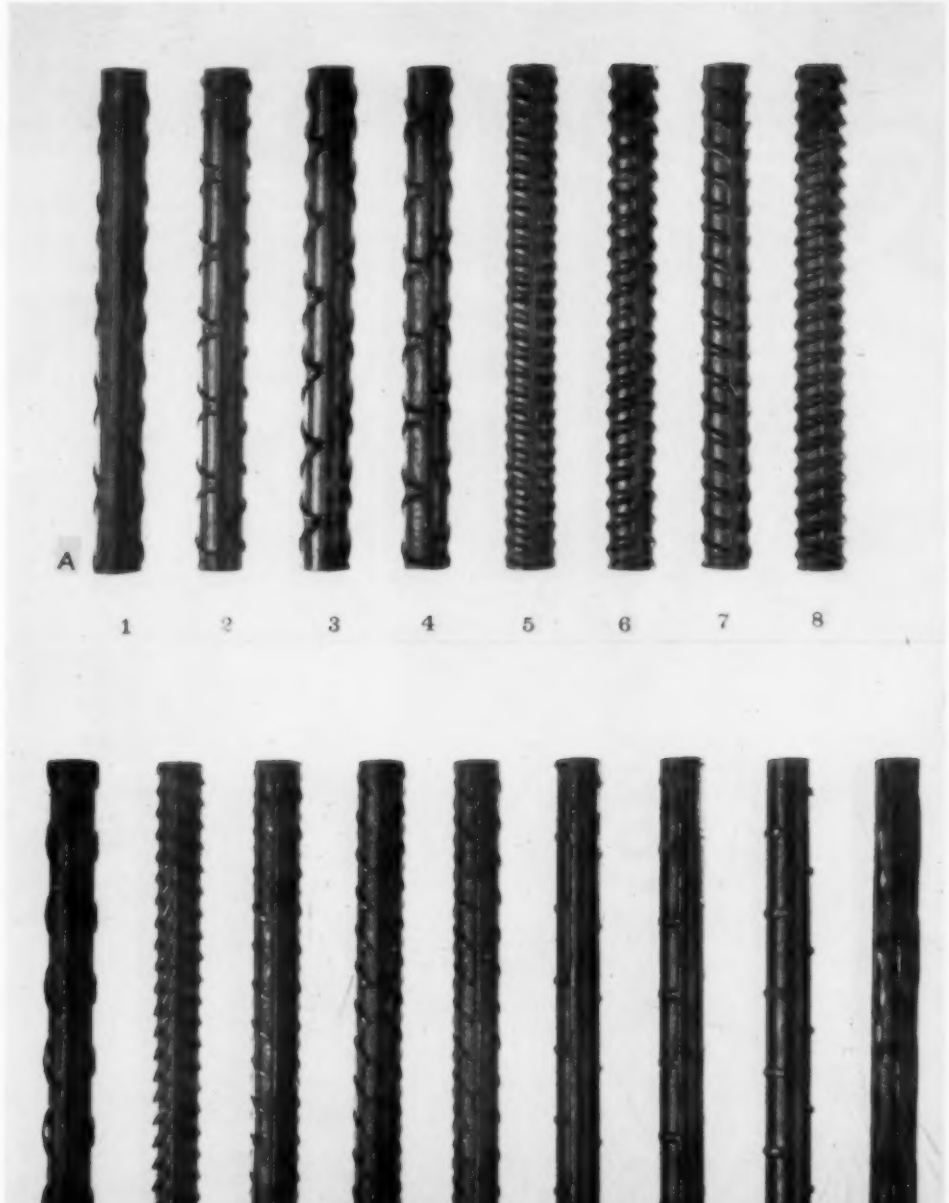

FIGURE 2.—*Types of bars tested.*

III. Description of Test Specimens

The pull-out specimens were 8 by 9 in. in cross section and of two lengths, 8 in. and 16 in.; the bars in these specimens were held rigidly in the molds during casting with the longitudinal ribs in a horizontal plane. Two specimens were cast in a mold 18 in. in depth, with one bar near the top and one near the bottom; the depth of concrete under the bar in the top position was 15 in., and 2 in. for the bar in the bottom position. Triangular steel strips welded horizontally to the interior sides of the molds at midheight scored the concrete blocks to permit their subsequent separation into two specimens.

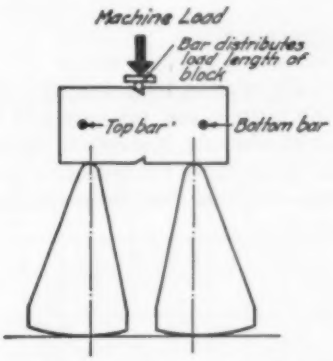

FIGURE 4.—*Method of breaking blocks to produce two pull-out specimens.*

The molds were made of heavy steel sections fabricated to permit stripping of the specimens without damaging the concrete, and the molds were sealed prior to casting to prevent leakage. The concrete was deposited in the mold in three layers and rodded in place.

The blocks were kept in moist storage in the molds after casting, and at the end of 3 days were removed and divided into two specimens by loading as a beam in a testing machine, as illustrated in figure 4. All blocks broke in a plane where scored, and the surface departed from a plane surface generally only to about the extent of the size of the coarse aggregate particles. The average breaking load was 1,660 lb/in. of length of specimen. The specimens were then placed in a moist room until tested at the age of 29 to 31 days.

IV. Testing Procedure

The pull-out specimens were tested in a 60,000-lb-capacity fluid-support, Bourdon-tube hydraulic machine, and the load was applied at the rate of about 2,000 lb/min, the dial gages being read without stopping the machine. The specimen was seated on a rubber cushion on two segments of a 2-in. base plate attached to the face of a spherical bearing block (fig. 5). Slip of the bar was measured with 0.0001-in. micrometer dial gages and the readings were estimated to 0.00005 in. At the loaded end, two dials, Nos. 1 and 2, were held by a steel bar firmly attached to the bottom face of the specimen by bolts screwed into a series of nuts cast in the specimen. The dial gages were in contact with the smooth surface of a steel yoke fastened to the reinforcing bar by three setscrews with cupped ends 1 in. below the surface of the concrete. The support bar for the dial gages and the yoke were free to move in a recess in the base plate. As load was applied, the average of the two dial-gage readings indicated the amount of movement of the point on the reinforcing bar at which the yoke was attached with reference to the lower face of the concrete. To give

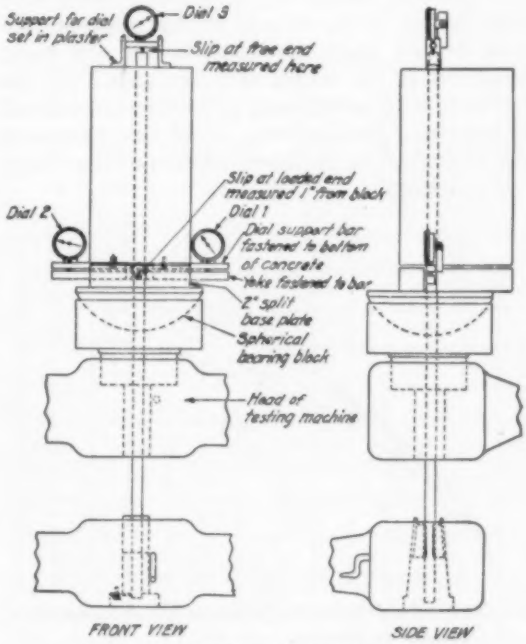
Support for dial set in plaster
Dial 3
Slip at free end measured here
Slip at loaded end measured 1" from block
Dial 2
Dial 1
Dial support bar fastened to bottom of concrete
Yoke fastened to bar
2" split base plate
Spherical bearing block
Head of testing machine
FRONT VIEW
SIDE VIEW

FIGURE 5.—*Specimen in testing machine.*

the slip at the face of the concrete (slip at the loaded end), the dial-gage readings were corrected for the elongation of the reinforcing bar in the 1-in. distance between the point of attachment of the yoke and the face of the concrete.

The slip at the free end was read directly from the dial gage mounted on a support, seated in plaster on the top of the specimen with the point of the dial resting on the planed end of the bar.

Initial dial-gage readings were taken at a machine load of 300 lb, then 600 lb, and readings at increments of 600 lb were taken until the machine registered 7,200 lb, and then at increments of about 1,200 lb until failure. The dial gages at the loaded end were removed as the stress in the bar approached the yield point or when a loosening of the support bar or yoke, due to the stretch in the bar or initial cracking of the concrete, made the readings of questionable value. Readings at the free end were continued until just before failure.

V. Results and Discussions

Tests in all cases were continued until failure of the specimen occurred, either by splitting of the concrete or by the bar pulling through the concrete. The typical splitting (79 percent of all specimens) was in a plane through the longitudinal ribs of the bar. The other specimens failed by splitting (13 percent) in a plane approximately at right angles to the plane through the longitudinal ribs. Seventeen specimens (8 percent) failed by the bar pulling through the concrete; these consisted of specimens containing bars No. 17 (with one exception), two each of Nos. 15 and 16, and one each of Nos. 11 and 13.

Twelve tests were made with each of the 17 bars with different patterns of deformations, three each with the bar in the top and bottom positions and with 8- and 16-in. embedments, the slip being measured at the loaded and free ends. All the test results for bars of each pattern were combined to arrive at a grand average, which thus represents the equivalent of 24 determinations of the stress-slip relationship.

The load-slip relation, as measured at the loaded end for both bottom and top bars and for the 8- and 16-in. embedments, is shown in figures 6, 7, 8, 9, and 10. Each curve represents, in general, the average data obtained from three specimens.

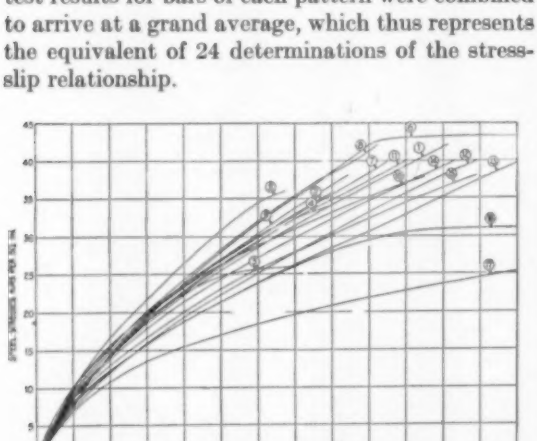

FIGURE 6.—*Load-slip curves for bottom bars embedded 16 in.*
Slip measured at the loaded end.

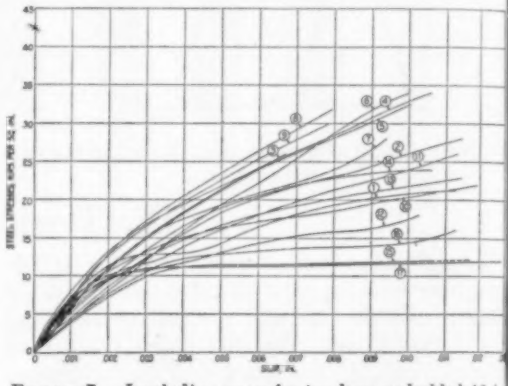

FIGURE 7.—*Load-slip curves for top bars embedded 16 in.*
Slip measured at the loaded end.

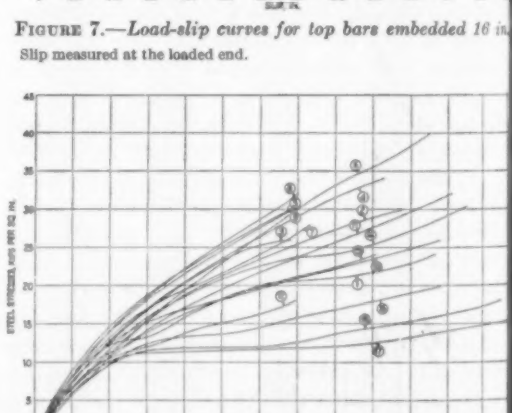

FIGURE 8.—*Load-slip for the average of bottom and top bars embedded 16 in.*
Slip measured at the loaded end.

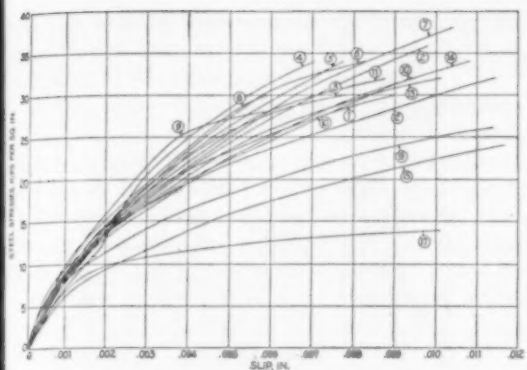

FIGURE 9.—*Load-slip curves for bottom bars embedded 8 in.*
Slip measured at the loaded end.

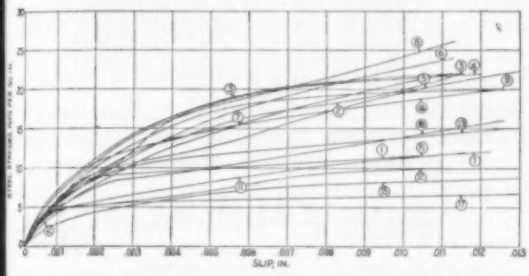

FIGURE 10.—*Load-slip curves for top bars embedded 8 in.*
Slip measured at the loaded end.

In the extensive literature dealing with the bond strength of reinforcing bars, the test bars have usually been rated by considering the stresses developed by the bars at some arbitrarily selected value of slip. In this investigation, an attempt was made to develop a method of rating bars that would take into account the stress-slip relationship for a considerable range of values of slip.

Load-slip curves of the bars of different designs show that some curves cross others. This means that one bar may have the highest stress for given slips along part of the curve, while the reverse may be true along another part of the curve.

Reinforced concrete has a wide variety of uses, ranging from members where the prime consideration is to keep cracks as narrow as possible, such as structures intended to confine liquids and avoid leakage or members exposed to attack by fumes or liquids that tend to hasten corrosion of steel, to those members where such conditions do not prevail and where deflection may not be a matter of particular concern. In the first case, a low value of design stress in the reinforcing steel is generally used, and in the other a high value. Between the extremes, other considerations may dictate the use of intermediate design stresses. A desirable concrete reinforcing bar would be one having a good bond resistance for all stresses within the range of probable use and up to the point of failure.

In this investigation, to determine the bars which could be expected to give the best bond resistance, it seemed logical to adopt a method for comparison that would rate the bars on the basis of average performance through a wide range of slip values. The method selected was to record the stress developed at several values of slip from the smallest at which readings were reliable up to the maximum slip developed by the majority of the bars. These stresses for each bar were totaled and the sum divided by the number of readings to obtain a figure indicative of the rating of the bar. These values may be used to indicate the bonding efficiency of the bars.

The values of slip at which the stresses were recorded are shown in table 3.

TABLE 3.—*Values of slip at which stresses were recorded*

Embedment	Position of bar	Measured at—	Slip
in.			*in.*
16	Bottom	Loaded end	0.0005, .001, .002, .003, .004, .005, .0075, and .01.
16	Top	do	0.0005, .001, .002, .003, .004, .005, .0075, and .01.
8	Bottom	do	0.005, .001, .002, .003, .004, .005, .0075, and .01.
8	Top	do	0.005, .001, .002, .003, .004, .005, .0075, and .01.
16	Bottom	Free end	0.00005 and .0001.
16	Top	do	0.00005, .0001, .0005, and .001.
8	Bottom	do	0.00005, .0001, .0005, and .001.
8	Top	do	0.00005, .0001, .0005, .001, .005, and .01.

The writer is of the opinion that this method, which is original insofar as he knows, is a reasonable one and gives a better basis for comparing bond performance than other methods heretofore employed.

The diagram in figure 11 represents, for slip at the loaded end, the rating of the bars for 16-in. embedment. The ordinates "steel stress" are the ratings used. In the vertical column for each type

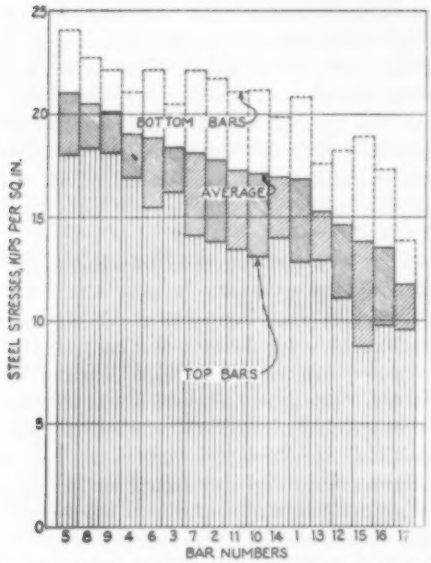

FIGURE 11.—*Rating for each bar corresponding to slips of 0.0005, 0.001, 0.002, 0.003, 0.004, 0.005, 0.0075, and 0.01 in. at the loaded end for 16-in. embedment.*

of bar, the maximum height of the column indicates the rating of the bottom bars. The top of the vertical hatched portion indicates the rating for the top bars, and the top of the diagonal hatched portion indicates the average rating for both top and bottom bars.

Figure 12 represents for slip at the loaded end the rating of the bar for 8-in. embedment, in a manner similar to figure 11.

Figure 13 represents the rating of the bars for slips at the free end. The ratings for 8- and 16-in. embedments are shown on one diagram in a manner similar to the diagrams for the loaded end. The solid line marked "G. A." represents the grand average of all the ratings for 8-in. embedment, 16-in. embedment, top bars, and bottom bars for slips at both the loaded and the free ends.

In figures 11, 12, and 13, the order in which the bars were arranged corresponds to the sequence of the average ratings of the bars with 16-in. embedment. Bars 8, 9, 6, 3, 4, and 5 showed the highest grand-average ratings, and in the order named, the difference between the extreme values of the grand averages being only about 11 percent. The average of these six exceeds the average of the remaining bars by 31 percent.

Considering the slip at both ends and for both embedments, the rating for all bars in the top

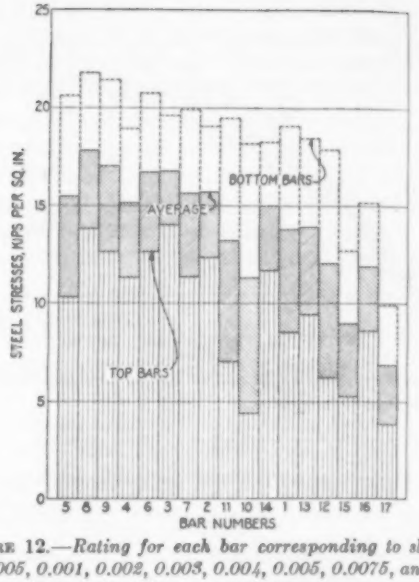

FIGURE 12.—*Rating for each bar corresponding to slips of 0.0005, 0.001, 0.002, 0.003, 0.004, 0.005, 0.0075, and 0.01 in. at the loaded end for 8-in. embedment.*

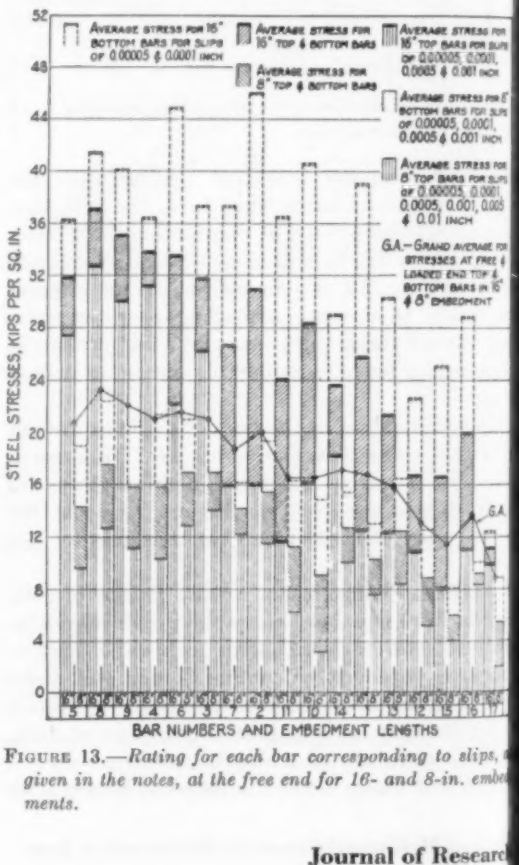

FIGURE 13.—*Rating for each bar corresponding to slips, as given in the notes, at the free end for 16- and 8-in. embedments.*

position was 56.8 percent of the rating for the bars in the bottom position. For bars 8, 9, 6, 3, 4, and 5, this ratio was 67.9 percent.

For all bars of the same type of design, Nos. 5, 6, 7, and 8, the ratio of the rating of the top bars to that of the bottom bars was 62.9 percent, and for all bars of the same general type, Nos. 1, 2, 3, 4, and 9, this ratio was 61.8 percent. The data from these tests indicate that, for bars cast in a horizontal position, the pattern of the deformations on the bar has little influence on the loss of bond strength due to settlement of the plastic concrete under the bar.

Although a detailed statistical analysis of the dispersion of the data was not made, an examination of the ranges of values of stress for slips greater than 0.003 in. at the loaded ends of bars indicated that a difference of less than 10 percent between the ordinates of any two of the curves of figures 6, 7, 9, and 10 is not positively significant. Similarly, differences of less than 1,500 lb./in.^{2} in the averages for the top and bottom bars shown in figures 11 and 12 or of less than 750 lb./in.^{2} in the grand averages shown in figure 13 may not be significant.

Bond resistance is influenced by several factors, including the average height of the deformations, the bearing area of the deformations, the shearing area of the concrete between the deformations, the inclination of the bearing face of the deformations, and the angle the deformations make with the longitudinal axis of the bar. Although in this series of tests it was not possible to compare bars in which only one of these factors was a variable, the graphs in figure 14 show the relation of these factors to the grand-average stress developed in the bars. As was to be expected, the presence of other factors obscured, to some extent, the relation between the grand-average stress and the variables shown in figure 14; nevertheless, the graphs illustrate an unmistakable trend in all cases, except the graph for the shearing area.

It is apparent that, in general, the grand-average stress increases with the bearing area of the deformations, their height, and the ratio of rating in the top bar to the rating in the bottom bar. It is of interest to note the similarity between the last two graphs named. The similarity of these graphs indicates that the height of deformations has an influence on the loss of bond strength due to the settlement of the plastic concrete under the bars. The graph illustrating the effect of the ratio of shearing area to bearing area shows that the bars with low grand-average stresses have an excessively high shearing area, and for bars with high grand-average stresses, this ratio is substantially constant between the values of 6 and 11.

The data from tests of bar No. 10 indicate that the inclination of the bearing face of the deformations is also a factor. Bar No. 10 has crescent-shaped deformations, and these point in the same direction on both sides of the bar. One face of the deformation is substantially normal to the axis of the bar, whereas the opposite face is inclined at an average angle of less than 30 degrees with the axis of the bar. Tests were made with some specimens in which the bar was pulled with the crescents pointing in the direction of pull, and others were made in which the bar was pulled with the crescents pointing in the opposite direction. The bearing area, shearing area, height of deformation, and the distance the deformations

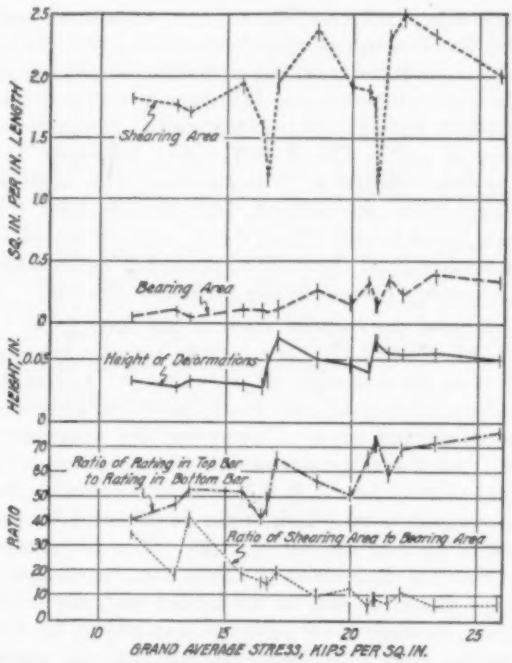

FIGURE 14.—*Effect of height and bearing area of deformations and shearing area of concrete between deformations and the ratio of stress in top bars to the stress in bottom bars on the grand average stress in bars.*

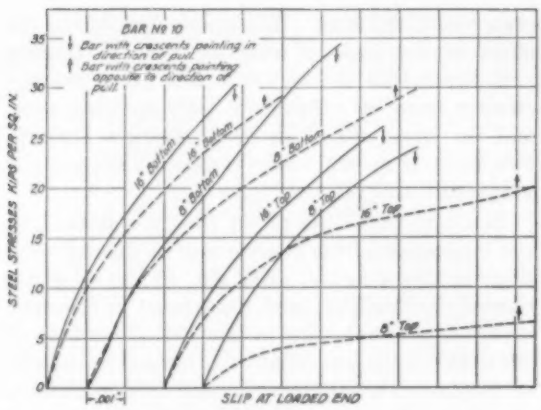

FIGURE 15.—*Load-slip curves for bar No. 10, determined for the loaded end.*

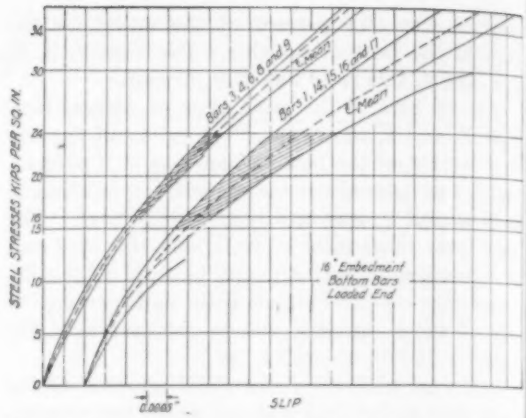

FIGURE 16.—*Load-slip curves for the five commercial bars (Nos. 1, 14, 15, 16, and 17) and the five best bars (Nos. 3, 4, 6, 8, and 9) in bottom position embedded 16 in., determined for the loaded end.*

extend around the bar were, of course, the same in all the tests of bar No. 10. Therefore, the only variable was the inclination of the face of the deformations and, to some extent, the shape of the concrete surface subjected to bearing stress. The load-slip relation for slip at the loaded end is shown in figure 15. The solid curves in each case are the average of specimens of bar No. 10, in which the bar was pulled in the direction in which the crescents pointed and the bearing on the deformations was against the face normal to the direction of pull. The dotted curves represent the opposite conditions. For all cases, 8-in. embedment, 16-in. embedment, bottom bars, and top bars, considerably higher values were shown when the bearing on the deformations was against the face nearly normal to the surface of the bar.

Five of the bars included in the tests (Nos. 1, 14, 15, 16, and 17) have been in commercial production for a number of years and are representative of deformed bars which have been generally accepted and used. Comparing the average of the grand average stresses of these five bars with that of bars Nos. 8, 9, 6, 3, 4, and 5 indicates the increase in bond which might be expected by the use of bars of the better types. The percentage of increase depends on the basis used for comparison. Based on slip at the loaded end, the minimum increase (21.6 percent) was shown by the bottom bars with 16-in. embedment; the maximum (64.7 percent) by the top bars with 8-in. embedment. The average increase of all bars at the loaded end was 39.8 percent. Based on slip at the free end, the minimum (47.1 percent) was shown by bottom bars with 16-in. embedment; the maximum (137.8 percent) by top bars with 16-in. embedment, and the average of all bars at the free end was 78.7 percent. The grand overall average increase was 60.1 percent.

The load-slip relation at the loaded end for the five bars with the highest ratings in this experiment and the group of five commercial bars cast in the bottom position for 16-in. embedment is shown in figure 16 and for 8-in. embedment in figure 17. The range of usual design stresses (16,000 to 24,000 lb/in^2.) is indicated by the cross-

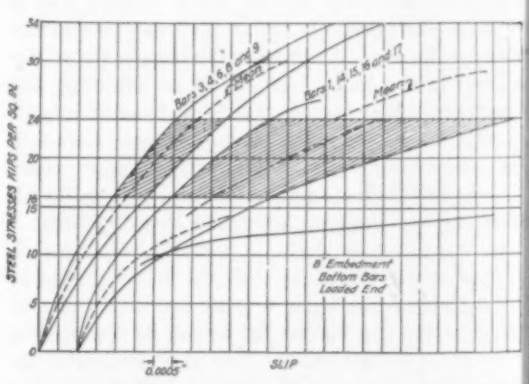

FIGURE 17.—*Load-slip curves for the five commercial bars (Nos. 1, 14, 15, 16, and 17) and the five best bars (Nos. 3, 4, 6, 8, and 9) in bottom position embedded 8 in., determined for the loaded end.*

hatched portion. The five bars with the highest ratings show much less variation than the commercial bars.

The data for the two groups of bars presented in figures 16 and 17 represent the results obtained with bars tested in triplicate. In those cases where one specimen of a set of three failed prematurely either by splitting of the concrete or slipping of the bar, the data for that bar were discontinued at the maximum load representing all three specimens; these "breaks" occur in the lower enveloping curves where they are indicated by discontinuities in the curves. The upper enveloping curves also show "breaks" that are due to the fact that the load-slip curves of the several bars in a given group intersected each other.

VI. Summary

The test specimens were of the pull-out type, in which the bars were cast in a horizontal position with length of embedment and depth of concrete under the bar varied. Provision was made for measuring the slip of the bar at both the loaded end and the free end of the bar.

The method used for evaluating the efficiency of the bars in bond resistance was based on the average performance for a range of slips as measured at the loaded end and at the free end for the bar with 2 in. and 15 in. of concrete under the bar and for 8- and 16-in. embedment.

The eight separate determinations for rating the bars gave, in general, consistent results. Considering the five bars rating highest in the grand average, one of the five rated highest in six of the determinations, one of the five rated second highest in all eight determinations, and one of the five rated third highest in all but one of the eight.

The average of the grand averages for bars Nos. 8, 9, 6, 3, 4, and 5 was approximately 60 percent higher than for the five commercial bars.

Bars 8, 9, 6, 3, 4, and 5 gave results which varied only about 11 percent from the highest. The five commercial bars gave results that varied by more than 41 percent from the highest.

In the top position, bars 8, 9, 6, 3, 4, and 5 were about two-thirds as effective in bond as in the bottom position.

Height of deformations appears as an important factor in determining the effect of the settlement of the concrete under the bar. The pattern of the deformation does not seem to be an important factor in determining the bond resistance.

The inclination of the face of the deformations is an important factor in determining the bond resistance.

Attention is called to the fact that the conclusions arrived at herein do not necessarily apply when the conditions are different from those that prevailed in this investigation.

The outline and general procedure for this series was prepared by R. R. Zipprodt, research engineer for the Committee on Reinforced Concrete Research, and acknowledgment is made of the very willing cooperation of all members of the Bureau staff, and in particular that of D. E. Parsons, chief of the Division of Mineral Products, and David Watstein, Materials Engineer, for their helpfulness and continued interest.

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Development of a Hydrochloric Acid Process for the Production of Alumina from Clay

By *James I. Hoffman, Robert T. Leslie, Harold J. Caul,* Lewis Jesse Clark, and John Drake Hoffman*

The development of a process for the extraction of alumina from clay and the construction of a pilot plant are described.

The process consists in (1) roasting clay at about 700° C, (2) digesting the roasted product with dilute hydrochloric acid, (3) filtering to separate the insoluble siliceous matter from the solution containing the aluminum and soluble impurities, such as iron and alkali salts, (4) concentrating the solution, (5) precipitating the aluminum as the hydrated chloride from the concentrated solution by adding hydrochloric acid gas, (6) removing the crystals of hydrated aluminum chloride, (7) washing the crystals to remove adhering impurities, (8) calcining the hydrated chloride to obtain alumina, and (9) recovering hydrochloric acid from the waste products at the end of the process.

The operation of the pilot plant shows that the process is feasible for the production of alumina from clay but that the alumina costs more than that produced from bauxite by the present well-known processes.

I. Introduction

The aluminum industry in this country depends a considerable extent upon bauxite shipped by a. Shortly after the United States declared war 1941, submarine warfare seriously interfered ith these shipments, and it became important to ilize domestic sources of alumina, of which clay the most abundant. At a conference in the ring of 1942 between Under Secretary of War obert P. Patterson, Assistant Attorney General ancis M. Shea, General Brehon Somervell, seph Y. Houghton of the Department of Justice, mah J. Briggs, Director of the National Bureau Standards, and James I. Hoffman, it was deed to construct and to operate a pilot plant at e National Bureau of Standards for the extrac- n of alumina from clay. The first part of the

*American Dental Association.

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work was done with War Department funds. Lt. Col. Henry M. Huxley acted as liaison officer between the War Department and the Bureau during the early part of the construction, and Capt. Robert Banks acted in the same role during the latter part of construction and operation. Both of these officers deserve much credit for their cooperation and helpful suggestions.

Preliminary plans for the plant were started in May 1942, but owing to extreme difficulty in obtaining delivery of equipment, actual construction could not be started until about January 1, 1943. On May 15, 1943, limited operation of the plant started, and on May 25, 1943, the first satisfactory alumina was produced. For the 2 years following, the plant was in almost continuous operation, with only occasional shut-downs for improvements and repairs.

The process consists in (1) roasting clay at about 700° C, (2) digesting the roasted product in dilute hydrochloric acid, (3) filtering to separate the insoluble siliceous matter from the solution containing the aluminum and soluble impurities such as iron and alkali salts, (4) concentrating the solution, (5) precipitating the aluminum as the hydrated chloride from the concentrated solution by adding hydrochloric acid gas, (6) removing the crystals of hydrated aluminum chloride, (7) washing the crystals to remove adhering impurities, (8) calcining the hydrated chloride to obtain alumina, and (9) recovering hydrochloric acid from the waste products at the end of the process.

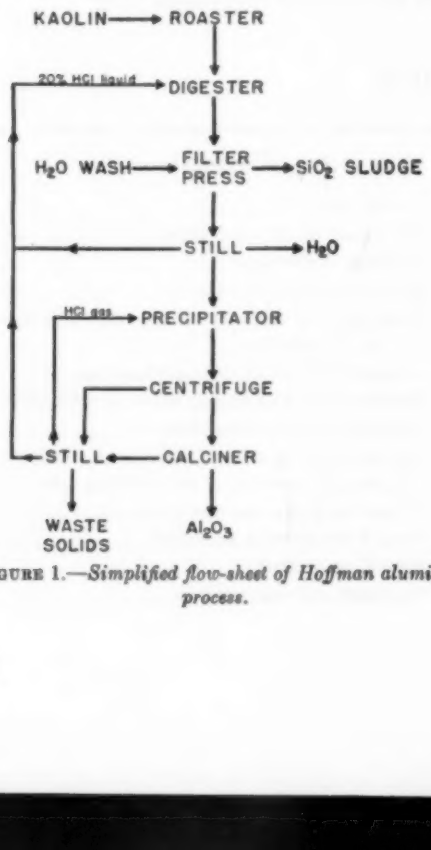

FIGURE 1.—*Simplified flow-sheet of Hoffman alumina process.*

The process in simplified form is outlined on the flow sheet, figure 1.

The preliminary experimental work centered around two main problems: (1) decomposition of clay with hydrochloric acid and (2) efficient separation of aluminum from iron and other soluble constituents of the clay. The alumina can be dissolved out of all clays by treatment with hydrochloric acid in closed containers at 300° C,[1] but the high pressures developed rendered this type of decomposition unsuitable for plant installation with the equipment available. Roasting the clay at about 700° C, according to the work of G. S. Tilley, A. W. Millar, and O. C. Ralston,[2] made it possible to dissolve the alumina in most clays at atmospheric pressure with dilute hydrochloric acid at approximately 100° C. The roasting procedure was therefore adopted so that the clay could be decomposed at atmospheric pressure.

For the separation of aluminum from iron and other constituents of clay that are soluble in hydrochloric acid, some procedure involving precipitation of hydrated aluminum chloride seemed best. By saturating a cool hydrochloric acid solution of the soluble constituents of clay with hydrochloric acid gas, only aluminum chloride hexahydrate, $AlCl_3.6H_2O$, is precipitated.[3] Practically all the other constituents remain in solution. This is in contrast with the separation of iron by extraction with ether, whereby only part of the iron is removed, and practically all other impurities remain with the aluminum.[4]

Instead of saturating the solution with hydrochloric acid gas to precipitate aluminum chloride, the aluminum can be separated as the chloride by partial evaporation. The aluminum chloride crystals thus formed have about the same solubility in the hot solution as in the cold, and laborato

[1] Edward Wichers, William G. Schlecht, and Charles L. Gordon, Prep... ing refractory oxides, silicates, and ceramic materials for analysis, by heat... with acids in sealed tubes at elevated temperatures, J. Research NBS ... 451 (1944) RP1621. A process based on decomposition at 250° to 300° C ... many attractive features if the difficulties concerning the high pre... be overcome.

[2] U. S. Bur. Mines Bul. 267, Acid processes for the extraction of alum... (1927).

[3] F. A. Gooch and F. S. Havens, Am. J. Sci. [4] **3**, 416 (1896).

[4] G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, Chemical analysis... iron and steel, p. 41 and 347, J. Wiley & Sons, New York, N. Y. (1931); J. ... Rothe, Stahl u. Eisen **12**, 1052 (1892).

xperiments showed that a continuous process can e based on crystallizing followed by centrifuging.[5] uch a process was contemplated early in the ork, but as no suitable crystallizer could be ought from the manufacturers or constructed ith the materials then available, it was decided o study first the precipitation of aluminum hloride by addition of hydrochloric acid gas, eserving the process involving crystallizing and entrifuging until a suitable crystallizer could be ought or constructed.

Recovery of hydrochloric acid by fractional istillation is by no means a new process, but it as found that the behavior of solutions of aluminum chloride in dilute hydrochloric acid differs markedly from that of a mixutre containing only water and hydrochloric acid. The ignition of aluminum chloride, sulfate, or nitrate to the oxide is common practice in the chemical laboratory and has never given analysts much difficulty. The process outlined in this discussion therefore does not involve new and mysterious reactions. In fact, the basic reactions involved in this process as well as in those pertaining to other acid processes for the extraction of alumina from clay, had been used and studied at the National Bureau of Standards in the analysis of bauxite, high-alumina refractories, aluminum metal, miscellaneous ceramic materials, and in the redetermination of the atomic weight of aluminum.[6]

[5] In the analysis of certain ceramic materials, from 1937-1942, the major ortion of the alumina was separated from solutions containing comparatively mall quantities of iron, lithium, and beryllium by evaporating the solution nd then freeing the crystals from mother liquor by decanting and centrifug- g. (Unpublished work of G. E. F. Lundell and James I. Hoffman at the ational Bureau of Standards.)

[6] G. E. F. Lundell and James I. Hoffman, Analysis of bauxite and of refractories of high alumina content, BS J. Research **1**, 91 (1928) RP5; Redetermination of the atomic weight of aluminum, J. Research NBS 18, 1 (1937) RP957.

II. Clays Used in the Pilot Plant

Experiments in the laboratory indicated that he process is applicable to nearly all clays, alough rather incomplete extraction of alumina sults in the case of diaspore clay or clays conaining high percentages of minerals, such as uscovite. Because of its abundance and accesibility, kaolin seemed to be the best raw material o use. Accordingly, the four kaolins described low were used in all the work in the pilot plant.

Pioneer crude kaolin.—This is a crude kaolin, lected for reasonable freedom from ferruginous aterial or other impurities that might cause bjectionable effects in ceramic products. At resent this material is regularly furnished to the eramic industry but is also available for the anufacture of alumina.

Air-floated kaolin.—Crude kaolin relatively free om mica and grit was crushed in a rotary crusher that none of the pieces was larger than 1 inch 3 inches. These were dried in a rotary drier til they contained about 10 percent of free isture, after which the lumps were crushed in roller mill, and the drying was almost instaneously completed with hot air. The crushed aterial was then projected into a controlled ward stream of air. The finer parts were blown ward, whereas the coarser parts either fell back o the crushing zone or into a separate exit for "rejects". The finer material thus constituted the air-floated kaolin.

Roller-mill rejects.—The roller-mill rejects were the coarser particles mentioned above and can be regarded as a byproduct of the air-floating process.

North Carolina surface kaolin.—The "surface kaolin" was obtained under our direction by Raymond E. Mothershead, of the National Bureau of Standards, from deposits near the surface in the vicinity of Raleigh, N. C. This type of material is entirely unfit for use in the paper or ceramic industry, but might be used under certain conditions to produce alumina. This kaolin was ground and sieved at the Bureau; no part of it was rejected. It should be noted that this surface kaolin is not typical of the regular North Carolina deposits. Samples taken 5 to 6 feet below the surface showed about the same composition as the pioneer crude.

Pioneer crude kaolin, air-floated kaolin, and roller mill rejects were furnished by Edward J. Grassmann, president of the Georgia Kaolin Co., Dry Branch, Ga.

Petrographic examinations of the four kaolins by H. F. McMurdie, Division of Clay and Silicate Products, National Bureau of Standards, showed that pioneer crude, air-floated, and roller-mill rejects contained a small percentage of muscovite,

which is practically insoluble in dilute hydrochloric acid. A much larger percentage was found in the surface kaolin. The air-floated kaolin had a maximum particle size of about 20 microns, whereas the other three contained much larger grains (up to 200 microns).

Measurements of bulk densities of the kaolins were made to supply information on storage space. The values recorded were obtained by heaping a can 12¼ inches high by 12 inches in diameter with kaolin, tapping lightly with a stick, raking the excess off the top with a straight lath, and then weighing. Such values will vary with the operator, but as all the determinations were made by the same person, the results shown in table 1 give information on comparative volumes of the different types.

TABLE 1.—*Bulk densities of the kaolins*

Type of kaolin	Bulk densities	
	Uncalcined kaolin as received	Calcined at 600° to 700° C (approx. 1,100° to to 1,300° F)
	lb/ft³	*lb/ft³*
Pioneer crude	59.9	59.9
Air-floated	36.7	35.5
Roller-mill rejects	55.0	56.2
North Carolina surface	52.5	50.0

The compositions of the four kaolins are shown in table 2. The results are given on the basis of the material as received.

Chemical analysis showed that all the kaolins contained ZrO_2, but that the amount did not exceed 0.1 percent. An important fact is that practically no titania is dissolved out of the calcined clay by any of the dilute acids mentioned. The maximum solubility observed was 0.03 percent with sulfuric, 0.025 percent with hydrochloric, and 0.01 percent with nitric acid.

The chemical analyses were made by Le Schubert, National Bureau of Standards.

Qualitative spectrochemical analysis by Harol R. Mullin showed that all the kaolins contained minor quantities (between 0.01 and 1 percent) o Ba, Cr, Li, and V, and traces (less than 0.01 per cent) of B, Co, Cu, Mn, Ni, Pb, Sc, Sn, Sr, Y, and Zn.

TABLE 2.—*Composition of kaolins*

Constituent	Roller-mill rejects	Pioneer crude	Air-floated	North Carolina surface
	Percent	*Percent*	*Percent*	*Percent*
Loss at 110° C	1.84	1.89	0.74	1.0
Loss at 1,200° C	14.3	15.0	14.4	7.7
Silica (SiO_2)	44.9	45.1	45.0	62.1
Aluminum oxide (Al_2O_3), total	36.0	36.8	38.4	24.8
Available Al_2O_3 *	32.6	35.7	37.9	15.6
Ferric oxide (Fe_2O_3)	1.0	.61	.43	.9
Titanium dioxide (TiO_2)	1.9	1.4	1.4	1.1
Phosphoric anhydride (P_2O_5)	.03	.03	.002	.0
Calcium oxide (CaO)	.25	.24	.06	.2
Magnesium oxide (MgO)	.26	.20	.05	.2
Sodium oxide (Na_2O)	.14	.07	.10	.4
Potassium oxide (K_2O)	.62	.14	.07	2.0

* Available alumina is determined as follows: Ignite 5.00 g of the sample at 700°±50° C for ½ hour. Cool the residue, transfer it to a flask having a capacity of 100 to 200 ml, add 50 ml of diluted hydrochloric acid (1 volume of HCl sp gr 1.18+1 volume of H_2O), cover the flask with a watch glass, and heat at about 100° C for 3 hours. Swirl the flask to stir up its contents every 10 minutes. Filter, wash the insoluble residue with water, and determine the alumina in the filtrate and washings. Substantially the same result for available alumina is obtained by the use of diluted sulfuric acid (1 volume of H_2SO_4 sp gr 1.84+3 volumes of H_2O) or diluted nitric acid (1 volume of HNO_3 sp gr 1.42+1 volume of H_2O).

III. Roasting of the Clays

Roasting to increase the solubility of the alumina in clay has been summarized by G. S. Tilley, R. W. Millar, and O. C. Ralston.[7] No extended research on roasting was done in the present work, but a few interesting observations will be recorded.

It can be said, in general, that the alumina in clays becomes more soluble in dilute acid (HCl, HNO_3, or H_2SO_4) if the clay is heated for a short period at 700° ±100° C before treatment with the acid. No particular advantage accrues from heating longer than one-quarter hour, nor is any harm done if the heating is prolonged to 1 hour. The wide range in temperature, (±100° C) is given because the most desirable temperature varies with different clays. Heating at too high a temperature, say 900° to 1,000° C, permanently renders the alumina insoluble in dilute hydrochloric acid. In practical work it is advantageous to determine the temperature at which best decomposition occurs for a given material.

[7] U. S. Bur. Mines Bul. 267 (1927).

It should be understood that in this discussion interest centers on the total alumina in clays and on the percentage of that alumina that can be dissolved in dilute acids near the boiling point at atmospheric pressure. Most of the work on this project was done with Georgia kaolin from which practically all the alumina can be thus extracted after roasting at 700° C. However, in preliminary work in the laboratory with two samples of diaspore clay (one from Missouri, the other from Pennsylvania) only about one-half of the alumina could be extracted by treatment with dilute hydrochloric or sulfuric acid at atmospheric pressure, regardless of time or temperature of roasting. Petrographic examinations of these samples showed two distinct mineral species, present in approximately the same ratio as the soluble and insoluble alumina. It is probable that the soluble portion was kaolin and the insoluble portion was diaspore. Diaspore, with or without roasting, can be decomposed by treatment with hydrochloric acid in a closed container at 300° C.[8]

Examination of about 15 clays showed that all contained a small quantity of alumina that does not respond to acid attack at atmospheric pressure after roasting. Nearly pure kaolin showed the best response, and the two diaspore clays mentioned, the poorest. Kaolin containing considerable quantities of muscovite occupied a middle position (see North Carolina surface kaolin, table 2). It is evident, therefore, that the nature of the raw material, as well as the roasting procedure and the digestion with acid, must be considered.

Unroasted kaolin containing about 1 percent of ferric oxide is nearly white. On roasting, it progressively becomes darker, up to a temperature in the neighborhood of 700° C, and then, on heating at increasing temperature, the light-brown color starts to fade. At 1,000° C the product is again nearly white. It is in the range of the maximum brown color that the best decomposition results on digestion with acid. This criterion serves in many cases as a practical means of telling whether the kaolin has been properly heated, but observation of the change in color cannot be substituted for a pyrometer because highly colored materials may not follow the rule.

If the roasting is properly done, all but about 0.5 percent of the water is driven off. Tests on five kaolins roasted at 700° C indicated an additional loss of only 0.4 to 0.5 percent on ignition at 1,200° C.

If the water of the kaolin is not reduced to 0.5 percent or less in the roasting process, recovery of alumina by digestion with dilute acid is quite unsatisfactory. For example, a sample of improperly roasted kaolin which retained 3.8 percent of its original water yielded 32.3 percent of alumina when treated with dilute hydrochloric acid, whereas a portion of the same kaolin by the same acid treatment yielded 37.8 percent of alumina after it was reroasted at 700° C to reduce its water content to 0.5 percent or less. A kaolin once properly roasted does not revert to its original insoluble form in a reasonably short time if it again comes in contact with water. For example, a 5-g portion of pioneer crude kaolin roasted at 700° C yielded 1.786 g of available alumina. A similarly roasted portion of the same kaolin was soaked in water for 4 days, then dried at 110° C, and similarly treated with dilute hydrochloric acid. The yield of alumina was 1.790 g. The difference in the quantity of alumina dissolved, of course, is insignificant, and similar results were obtained with other kaolins. The roasted kaolin, after soaking with water 4 days, retained 3.5 percent of water when dried at 110° C. This reabsorbed water, although retained at 110° C, did not decrease the amount of alumina extracted, whereas a decided decrease in soluble alumina resulted from incomplete removal of the *original* water of constitution. Thus two samples of roasted kaolin might each show 3.5 percent of water. One might have been improperly roasted so that this amount of its *original* water remained. The other might have been properly roasted at 700° C to remove all of its original water and then have been exposed so that it picked up 3.5 percent of moisture. The one retaining its *original* water of constitution would show the lower percentage of available alumina.

In the pilot plant a three-hearth Wedge furnace was used for the roasting. The hearths were 2 feet 3 inches in diameter by 9 inches in height, inside dimensions. The total roasting area of the three hearths was 10 square feet. The furnace was similar in its general construction and operation to the Nichols Herreshoff furnace shown in figure 7, except that the flame in the Wedge furnace was

[8] Charles L. Gordon, William G. Schlecht, and Edward Wichers, J. Research NBS **33**, 457 (1944) RP1622.

in direct contact with the kaolin, whereas the Nichols Herreshoff furnace is muffle-fired. The Wedge furnace [9] was obtained from the Bethlehem Foundry & Machine Co., Bethlehem, Pa. The usual type of rotary kiln would probably serve equally well.

The center shaft and rabble arms were made of cast iron and were cooled in the conventional way by forcing a stream of cool air through the shaft and arms. The rabble teeth were also made of cast iron. The kaolin used required roasting at about 700° C (1290° F) for best extraction of the alumina with acid. With the heat necessary to maintain the kaolin at this temperature, the cast-iron rabble arms had a tendency to sag and cause breakages. If this type of furnace is to be used in large installations, the rabble arms and bolts, and possibly the center shaft, should be of rugged construction or be made of metal that will not warp or sag.

The rate of passage of kaolin through the furnace can be controlled by the speed of the rabble arms, provided that a supply of kaolin is always available at the intake at the top of the furnace. An electric vibrating feeder [10] was used to insure a continuous flow and operated satisfactorily with the pioneer crude, the roller-mill rejects, and the North Carolina surface kaolin. It failed occasionally with the air-floated kaolin because this fluffy type of material packed and would not fall out of the feeding hopper into the furnace. With a large hopper and larger openings, this packing could not stop the flow. No particular significance is to be attached to this difficulty because air-floated kaolin is not likely to be used in this process on a commercial scale.

The rate of output of calcined clay per hour which generally resulted in the highest percentage of available alumina was as follows for the three-hearth furnace described: Air-floated, 25 lb; pioneer crude, 60 lb; roller-mill rejects, 60 lb; and North Carolina surface kaolin, 55 lb. At the maximum speed of the rabble mechanism, the output per hour was: air-floated, 50 lb; pioneer crude, 100 to 120 lb; roller-mill rejects, 100 to 120 lb; and North Carolina surface kaolin, 100 lb.

In many cases the roasting did not reduce the combined water to 0.5 percent or less, and consequently complete extraction of the alumina was not possible. Three ways of attaining better dehydration are open, namely, (1) increasing the temperature, (2) decreasing the rate of feeding the kaolin, or (3) increasing the number of hearths of the furnace. Slow feeding aids the dehydration but limits the output. Changing from a three-hearth to a six-hearth furnace undoubtedly results in an improvement of the calcined product. For example, a 200-lb portion of kaolin that had been calcined at an average temperature of 1,220° F was recalcined at an average temperature of 1,210° F. There was an additional loss of 2.2 percent of water, and the soluble alumina was increased by 4 percent (from 25.3 to 29.3 percent). Experience, therefore, indicates that, if a furnace of the Wedge type is to be used, it should be constructed with metal or ceramic parts that do not warp or sag if operated at 1,300 to 1,400° F, and that it should contain six hearths so that slow feeding need not retard the output.

The heat required for proper roasting was approximately 1,690 Btu/lb of roasted kaolin.

[9] This type of furnace is described by Andrew M. Fairlie in "Sulfuric acid manufacture" (Reinhold Publishing Corporation, New York, N. Y., 1936) and will, therefore, not be described in detail here.

[10] Purchased from the Syntron Co., Baltimore, Md.

IV. Decomposition of the Clays

After roasting the kaolin at about 1,300° F, it was digested at 212° to 220° F with hydrochloric acid, sp gr 1.07 to 1.10, for about 3 hours. The digester was made of Haveg 41,[11] and is illustrated in figure 2.

The stirrer, *A*, shown in the figure had a blade, *G*, 24 by 3½ inches, and was driven by a totally enclosed motor. A stirrer speed of 60 rpm was found to give ample agitation. Heat was introduced by means of 11 Karbate [12] bayonet heaters, *F*, supplied with steam at a gage pressure of about 30 lb/in.^{2} Each heater had a surface of about 950 square inches in contact with the solution.

[11] Haveg 41 is molded from a mixture of a special acid-digested asbestos and a synthetic phenolformaldehyde resin. It is manufactured by the Haveg Corporation, Newark, Del.

[12] Karbate is a material consisting of carbon or graphite with binder. Carbon-base has low heat transfer; graphite-base has high heat transfer. Karbate is manufactured by National Carbon Co., New York, N. Y.

See table 3 for the rate of transfer of heat through the bayonets.

The usual charge was 200 lb of kaolin and 200 gal of acid because such a charge allowed ample excess of acid over that required to dissolve the alumina, iron oxide, and other soluble portions of the kaolin. The acid was first heated to 175° to 195° F, and then, while the steam was turned off, the entire charge of calcined kaolin was dropped into the acid through the opening, *B*, (fig. 2)

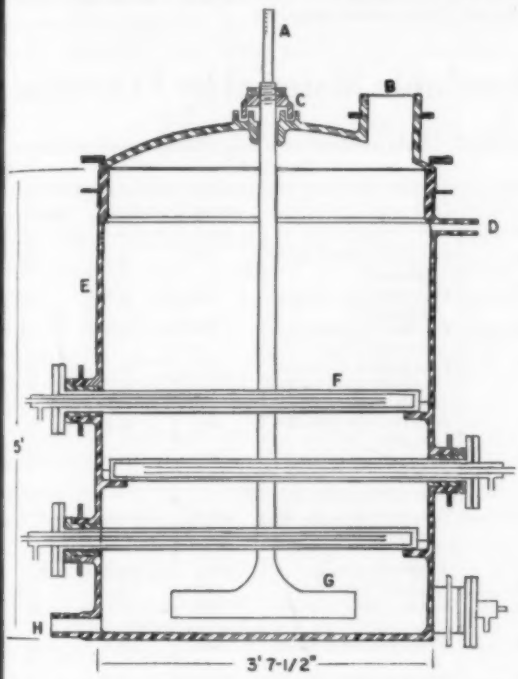

FIGURE 2.—*Digester for decomposing clay with hydrochloric acid.*

A, Stirrer shaft; *B*, inlet for clay; *C*, vapor seal; *D*, inlet for acid; *E*, tank made of Haveg 41; *F*, Bayonet heater made of Karbate No. 28; *G*, pitched blade of stirrer; and *H*, outlet for digested material.

which was loosely covered after the kaolin was introduced. *C* is a seal to prevent escape of acid, *D* is the inlet for the acid, and *H* is the outlet to the filter press.

The heat of reaction between the soluble constituents of the kaolin and the acid usually raised the temperature of the slurry to slightly above 212° F in the course of 45 minutes. This rise was more rapid with very finely divided kaolin, such as the air-floated, than with the coarser type, such as

TABLE 3.—*Thermal data on decomposition of kaolin*

(a) Specific heat of acid used for decomposing kaolin in run 51 was calculated from the following data:

Water equivalent of digester (Btu required to raise temperature of digester 1° F)	410
Volume of acid, gal	200
Specific gravity of acid at 26° C	1.075
Al_2O_3 content, lb/gal	0.07
HCl content, lb/gal	.87
Heat added (based on weight of condensed steam) Btu	68,500
Rise in temperature, ° F	31.5
Time of heating, min	23
Rate of cooling to surroundings, ° F/min	0.115
Corrected rise in temperature, ° F (31.5+23×0.115)	34.1

$$\text{Specific heat, Btu/gal (for 1 deg F)} = \frac{\text{Heat added} - (\text{rise in temperature} \times \text{water equivalent of digester})}{\text{Corrected rise in temperature} \times \text{volume of acid}} = 8.0$$

(For temperatures between 140° and 175° F)

Similar data were taken for five other runs. Values for the specific heat of the acid, ranging from 7.9 to 8.5, were obtained. The average of all the values is 8.1 Btu/gal (for 1 deg. F).

(b) The specific heat of kaolin was determined as follows:

Two hundred pounds of calcined kaolin, cooled to a definite temperature, was dropped into 200 gal of water at an accurately measured temperature (about 190° F). From the decrease in temperature of the water, values for specific heat of kaolin were calculated. Correction for heat capacity of tanks and for dissipation of heat were made as in the determination of the specific heat of the acid for digestion of the kaolin. (See (a) above.) The average of four values is 0.23 Btu/lb for 1° F. Although this value is useful for plant calculations, it is not to be regarded as an accurate value for the specific heat of raw or roasted kaolin.

(c) Heat of reaction of roasted kaolin with acid in run 54 was calculated from the following data:

Average temperature of calcination of roller-mill reject kaolin (°F)	1,254
Weight of kaolin, lb	213
Volume of acid, sp gr 1.063 at 27° C, gal	200
HCl content of acid, lb/gal	0.76
Al_2O_3 content of acid, lb/gal	.08
Temperature of acid when kaolin was added, °F	186.8
Temperature of kaolin when added to acid, °F	89.6
Rise in temperature during reaction, °F	30.6
Time of reaction, min	45
Rate of cooling, °F/min	0.11
Corrected rise in temperature caused by reaction, °F, (30.6+45×0.11)	35.6
Heat added by steam to products of reaction after completion of reaction, Btu	49,900
Rise in temperature of products and digester during heating with steam after completion of reaction, °F	18
Time of heating by steam, min	21
Corrected rise in temperature of products, °F, (21×0.11+18)	20.3
Heat capacity of products and digester, Btu/° F, 49,900/20.3	2,458
Heat of reaction of 200 gal of acid with 213 lb of kaolin, Btu. 35.6×2458+0.2×213×(186.8−89.6). (Corrected rise in temperature caused by reaction×heat capacity of products and digester+specific heat×wt of kaolin×rise in temperature of kaolin).	91,646
Al_2O_3 dissolved, lb	63.7
Heat evolved per pound of Al_2O_3 dissolved, Btu	1,439

Similar data were taken in five other runs. The values ranged from 1,348 to 1,445 Btu. The average of all values is 1,396 Btu/lb of Al_2O_3 dissolved.

(d) The rate of transfer of heat through Karbate No. 28 bayonets averaged 0.040 Btu in 1 minute for each square inch of surface for 1° F difference in temperature between steam on inside and solution on outside. The measurements were made at a steam pressure (gage) of 25 lb/in.², and the walls of the Karbate heaters were 7/16 in. thick. The temperatures of the solutions surrounding the heaters ranged between 140° and 197° F.

(e) Total heat required for decomposition of kaolin 902 Btu/gal of acid. This is an average of five values actually obtained in the operation of the plant. Insulation of digester tanks would reduce this value somewhat.

the roller-mill rejects. The charge was kept at a temperature of 212° to 220° F for 2 to 3 hours by means of the Karbate heaters. Very little heat was required to maintain this temperature. Actually, very little alumina was dissolved after the first hour of digestion, and, for commercial operation, digestion for 1 hour is sufficient. An approximate determination of the heat evolved in the reaction between the kaolin and acid was made and was found to be about 1,400 Btu/lb of alumina dissolved. This value corresponds fairly closely to the theoretical [13] value for the solution of Al_2O_3 in HCl, which suggests that, after roasting, the constituents of kaolin act as if they existed as separate compounds.

Thermal data on decomposition of kaolin are given in table 3.

[13] According to the data in "Thermo-chemistry of chemical substances," by F. R. Bichowsky and F. D. Rossini (Reinhold Publishing Corporation, New York, N. Y., 1936), the heat of reaction between Al_2O_3 and HCl is 1,426 Btu/lb of Al_2O_3 in 10-percent HCl and 1,371 Btu/lb of Al_2O_3 in 1-percent HCl. As the final solutions in this work were quite complex and contained hydrochloric acid in concentrations somewhere between 1 and 10 percent, exact theoretical values are not to be expected.

V. Separation of Silica and Other Insoluble Material by Filtration

The slurry in the digester was cooled to 130° to 140° F by turning off the steam and circulating cooling water through the bayonet heaters. From the digester the cooled slurry was pumped into a filter press by means of a Duriron sludge pump, which maintained a pressure up to 20 lb/in². The frames (24 by 24 by 2 in.) and plates were made of pine, and the cloths were made of Vinyon (a fabric compounded of vinyl acetate and vinyl chloride). After all the slurry was pumped into the press, the filter cake was blown dry with compressed air, after which it was washed with water. About 160 gal of filtrate were obtained, and usually a little over 100 gal of water were used for washing.

The data on the three digestions and filtrations given in table 4 illustrate the performance of the digester and filter press.

TABLE 4.—*Data on digestion of clay, filtration, and washing*

		Run 60	*Run 61*	*Run 65*
1	Weight of calcined kaolin used, lb.	200	200	250
2	Volume of hydrochloric acid used, gal.	200	200	250
3	Al_2O_3 in acid, lb	15.2	16.2	30
4	Available Al_2O_3 in kaolin, lb.	63.6	61.0	88
5	Alumina to be expected in filtrate and washings (No. 3+No. 4),[1] lb.	78.8	77.2	118
6	Free HCl in acid used for digestion, lb.	215	155	275
7	Al_2O_3 in filtrate (no washings), lb.	66.6	67.6	103.5
8	Free HCl in filtrate (no washings), lb.	70.0	22.6	70.0
9	Al_2O_3 in first 50 gal of washings, lb.	9.5	7.5	10.5
10	Free HCl in first 50 gal of washings, lb.	9.1	3.6	10.2
11	Al_2O_3 in second 50 gal of washings, lb.	2.0	1.6	2.5
12	Free HCl in second 50 gal of washings, lb.	2.3	1.5	3.5
13	Total Al_2O_3 in filtrate and washings (No. 7+No. 9+No. 11) lb.	78.1	76.7	116.5
14	Al_2O_3 dissolved (No. 13−No. 3) lb.	62.9	60.5	86.5
15	HCl consumed in dissolving Al_2O_3 No. 6−(No. 8+No. 10+No. 12) lb.	133.6	127.3	191.3
16	HCl equivalent to the Al_2O_3 dissolved (No. 14) lb.	132.9	129.8	185.6
17	Weight of sludge, lb	217	210.0	235
18	Volume of sludge, ft.³	2.7	3.0	3.9
19	Weight of H_2O in sludge, lb.	95.7	76.1	91
20	Weight of solids in sludge, lb.	121.3	133.9	144
21	Weight of soluble Al_2O_3 in sludge, lb.	0.22	0.08	0.45
22	Weight of free HCl in sludge, lb.	.22	.21	.69
23	HCl combined with Al_2O_3 in sludge, lb.	.47	.17	.97
24	Total loss in sludge	0.22 lb Al_2O_3 + 0.69 lb HCl.	0.08 lb Al_2O_3 + 0.38 lb HCl.	0.45 lb Al_2O_3 + 1.57 lb HCl.
25	Percentage of available Al_2O_3 recovered (No. 14/No. 4)×100.	98.9	99.1	98.3

[1] Numbers in parentheses refer to the numbers in the first column of this table.

As charged into the digester, the ignited kaolin contained the available alumina indicated. Because of the difficulties previously mentioned in maintaining the roasting furnace in good operating condition at 1,300° F or higher, these kaolins were heated at a slightly lower temperature than that required to expel all the water of constitution,

with the consequent failure to render all the alumina soluble. With proper roasting, the available alumina would have been about 38 percent of the weight of the calcined clay. The alumina in the acid is a result of incomplete precipitation in previous runs and the fact that this dilute acid was used to wash crystals of aluminum chloride out of various parts of the system. This is normal procedure.

Under proper operating conditions, filtration usually required 1 hour, and the washing operation required another hour. Clear filtrates were readily obtained, and filter aids did not improve the procedure sufficiently to warrant their use. The low silica content of the alumina produced is good evidence that the filtering operation was satisfactory.

During the operation of the plant, it was found that filtration and washing required progressively more and more time, until finally 3 hours were consumed. It was then discovered that the cloths were covered with a thin film of grease (probably from the packing in the sludge pump). After washing the dried cloths in mineral spirits or gasoline, the normal time schedule of 1 hour for a filtration was reestablished.

VI. Concentration of Filtrate and Washings

The filtrate and washings were evaporated to a relatively small volume to minimize the quantity of hydrochloric acid gas required in the next step to precipitate the aluminum as the hydrated chloride, $AlCl_3.6H_2O$. A concentrated solution having a specific gravity of about 1.30 and containing about 1.20 lb of Al_2O_3/gal is satisfactory. For this concentration a Haveg still with a capacity of 250 gal was used. The still was heated by means of bayonet heaters similar to those in the digester (fig. 2). The vapor passed up through a Haveg rectifying column 10 feet high and 24 inches in inside diameter. This column was packed with 1-inch ceramic raschig rings. From the top of the column, the vapors passed into a water-cooled condenser (Karbate pipes surrounded by water). The distillate was tapped from the bottom of the condenser.

Provision was made for refluxing so that water or dilute acid which first distilled could be pumped back to the top of the rectifying column. In a typical distillation, about 40 percent of the flow of the distillate (consisting of water at first) was pumped back to the top of the rectifying column as refluxing liquid. In regular practice the refluxing was discontinued as soon as the desired amount of water was removed from the system or when the concentration of acid in the distillate became too high to permit it to be discarded (see table 4). The water distillate was discarded, and the acid distillate was retained for future decomposition of clay.

If a solution containing only water and hydrochloric acid is distilled, a point will be reached where the distillate consists of constant-boiling acid, specific gravity about 1.10. Continued distillation will not change the composition of the distillate. However, if a salt such as aluminum chloride is present, the usual constant-boiling acid will never be obtained. The behavior of such solutions is illustrated in figure 3. The curve marked *O* represents data obtained by distilling at atmospheric pressure without reflux a solution having the following properties and composition:

Total chlorides	87.76 g/liter, equivalent to 90.4 g of HCl/liter.
Chloride combined with Fe	1.67 g/liter.
Chloride combined with Al	60.45 g/liter.
Free chloride	25.64 g/liter, equivalent to 26.40 g of HCl/liter.
Specific gravity at 18° C	1.086.
Boiling point	103° C.

This was a portion of filtrate and washings in run 48, and is typical of all the solutions that were concentrated prior to the precipitation of the aluminum chloride with hydrochloric acid gas. The curve marked Δ represents data obtained by distilling a solution containing only water and hydrochloric acid. The hydrochloric acid content was 90.4 g/liter. The total chloride content of both solutions was therefore the same, and the same distilling apparatus was used for both. The point *A* on curve *O* where all free acid has been removed from the still happens to appear near the maximum in this particular case, but this should not be regarded as true for all solutions because

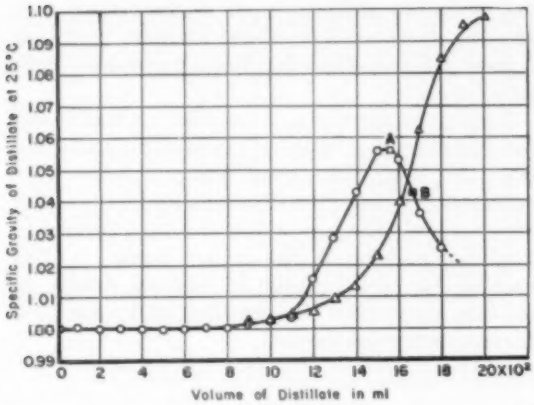

FIGURE 3.—*Comparison of distillates obtained from (1) a dilute hydrochloric acid solution containing aluminum chloride and (2) dilute hydrochloric acid alone.*

Curve O, dilute HCl containing aluminum chloride; curve Δ, dilute HCl alone; *A*, point where all free HCl was distilled (temperature of still pot 117 to 120° C); *B*, point where crystals of $AlCl_3.6H_2O$ started to separate (temperature of still pot 124° C).

the position of the point at which all free acid has been distilled varies somewhat with the composition of the solution. The point *B* at which crystals first separate in the distilling flask usually occurs shortly after all free hydrochloric acid has been distilled.

The solution when crystals start to separate boils at about 124° C (255° F), and the concentration of aluminum chloride corresponds approximately to that of water saturated with aluminum chloride. Solubility of aluminum chloride in water changes only slightly with temperature. As far as this process is concerned, the significance of the two curves is that, in the concentration of the filtrate and washings containing acid and aluminum chloride, hydrochloric acid of a higher specific gravity than 1.06 is never obtained as distillate. All the actual runs made during the operation of the plant yielded data in conformity with the curves of figure 3. In the plant, concentrating the solution was always stopped soon after the maximum of the curve was passed. This maximum varies with original concentrations. Thermal data on concentration of filtrate and washings are given in table 5.

TABLE 5.—*Data on concentration of filtrate and washings*

(a) Rate of distillation:
With a reflux ratio of 50 percent (that is, when 50 percent of the distillate was pumped back to the top of the still column during distillation) water was distilled at the rate of about 0.6 gal/min. With no reflux, water was distilled at the rate of about 0.75 gal/min. Acid was always distilled without reflux. The average rate was about 0.3 gal/min.

(b) Effect of reflux on distillation:
With the reflux ratio mentioned, about 30 percent more water was obtained as distillate than with no reflux. For example, in a certain distillation 83 pct of "water" distillate was obtained without reflux; by pumping all the distillate back into the still and then distilling as before but with a reflux ratio of 46 percent, 119 gal of water distillate was obtained. The point at which "water" distillation was regarded as complete was when the specific gravity of the distillate as it flowed from the condenser rose to 1.002.

(c) Concentration of acid in "water" distillate:
The "water" distillate, collected from the beginning of distillation up to the time when the specific gravity reached 1.002, contained 0.003 lb of HCl/gal.

(d) Composition and properties of concentrate: (material remaining in still is referred to as concentrate).
1. Free HCl content.—Practically no free HCl remains—seldom more than 0.1 lb HCl/gal (see fig. 3).
2. Al_2O_3—Average of 0.11 lb of Al_2O_3/lb of concentrate or about 1.2 lb/gal.
3. Specific gravity, 1.28 to 1.32.
4. Volume.—Under operating conditions described, the volume of concentrate is approximately 20 percent of the original volume of filtrate and washings.
5. The weight of the concentrate is about 25 percent of the weight of filtrate and washings.
The volume of concentrate averages approximately one-fifth that of the filtrate and washings; the weight of the concentrate averages approximately one-fourth that of the filtrate and washings. These values vary rather widely. For examples, in run 60, 280 gal of filtrate and washings, sp gr 1.09, weighing 2,527 lb, yielded 56 gal of concentrate, sp gr 1.311, weighing 612 lb; and in run 63, 285 gal of filtrate and washings, sp gr 1.101, weighing 2,615 lb, yielding 65 gal of concentrate, sp gr 1.312, weighing 711 lb.

(e) Total heat required to produce concentrate from filtrate and washings Btu/lb of concentrate 4.0

(f) Heat required to bring filtrate and washings to distilling temperature (uncorrected for heat losses of still to surroundings) Btu/gal for each ° F, 19.8

(g) Velocity of vapor in still column, ft³/min for each square foot of cross section of column ..... 35 to 6

VII. Precipitation of Aluminum Chloride, $AlCl_3.6H_2O$

After concentrating the filtrate and washings in the manner described in the previous section, the cooled concentrated solution was pumped into the tank *G*, of the precipitator (fig. 4), which had a capacity of 125 gal.

By means of a glass pump located below the level of outlet *H*, the solution was circulated by pumping it to the top of the *unpacked* tower *D* (9 ft. by 18 in.) mounted above tank *G*, as illustrated in figure 4. The solution thus fell against the stream of hydrochloric acid gas which entered at *E* at the bottom of tower *D*. Any unabsorbed gas passed out at *C* and was recirculated. The perforated plate *B* at the top of the tower was

FIGU

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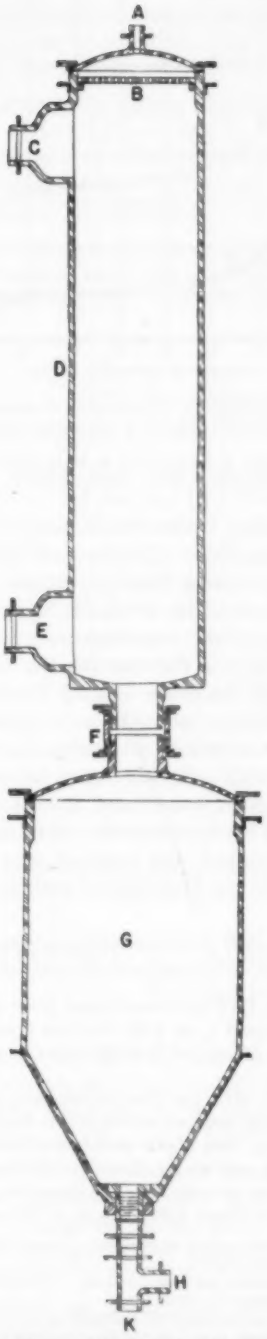

FIGURE 4.—*Precipitator for aluminum chloride.*

inserted to break the stream of liquid to expose more surface to the opposing flow of gas. A rapid stream of liquid is desirable because better absorption is obtained, and there is less trouble from clogging of gas inlets and outlets by deposition of crystals of aluminum chloride. A desirable rate of circulation of solution through this tower is about 30 gal/min. Satisfactory results were obtained in this unit by continuous operation at full capacity, but clogging of inlets and outlets by crystals of aluminum chloride often resulted if the unit remained out of operation for any extended period.

The hydrochloric acid gas was generated in still *B* (fig. 8) from solutions containing hydrogen chloride in a sufficiently high concentration to yield the gas on boiling. The three sources of such concentrated acid were (I) filtrate from crystals of aluminum chloride obtained in a previous precipitation, (II) acid of sp gr 1.18 to 1.20 formed by cooling the gases issuing from the Herreshoff furnace during the ignition of aluminum chloride and absorbing the hydrochloric acid gas in cool constant-boiling hydrochloric acid, (III) Carboy acid, specific gravity about 1.17, supplied to make up for losses incurred in operating the plant.

Hydrochloric acid gas is absorbed more rapidly at low than at high temperatures. Because of the heat developed by dissolving the hydrochloric acid gas, it is necessary to cool the solution.[14] This is most conveniently done by interposing a cooling system between the circulating pump and the top of the absorption tower. Two types of cooler were used. One was made of Karbate No. 28 pipe; the other was made of Pyrex heat exchanger pipe. Both were constructed with sweep return bends and immersed in running water. With the cooler made of 30 feet of 1-inch glass cooling pipe, the flow of liquid was so valved that about one-third of it passed through the cooler and two-thirds in a straight line from pump to top of tower. With city water at a temperature of 60° to 70° F, a satisfactory temperature was maintained in the solution in precipitator tank *G*, figure 4. Dimensions and operation of the cooling unit are necessarily quite flexible because of variations in temperature and rate of flow of hydrochloric acid gas

[14] The heat to be dissipated was actually found to be about 500 Btu/lb of HCl absorbed. This determination was made by measuring the quantity of water passing through the cooler and its rise in temperature.

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as well as temperature and rate of flow of cooling water. For effective absorption, the temperature of the solution in tank *G* must be maintained below 80° F, preferably below 70° F. Cooling capacity should be calculated on the basis of dissipation of at least 500 Btu/lb of hydrogen chloride absorbed.

During a part of the operation of the plant, two absorption units were used so that the unabsorbed hydrochloric acid gas from the unit nearing complete saturation could be absorbed in the second unit containing fresh solution.

At the beginning of the saturation with hydrochloric acid gas the concentrated solution in the precipitator has a specific gravity of 1.30 to 1.32 and contains about 1.20 lb of Al_2O_3/gal. The specific gravity of the solution drops as the aluminum chloride is precipitated. Usually the precipitation is discontinued when the aluminum content drops to 0.1 lb of Al_2O_3/gal. This corresponds to a specific gravity of 1.18 to 1.20 in the supernatant liquid. The drop in specific gravity of the solution corresponding to the drop in its alumina content is illustrated in figure 5. It is obvious that the progress of the precipitation is indicated approximately by the specific gravity of the solution, but actual determinations of alumina were made before final disposal of the solution.

Distilling the available hydrochloric acid gas out of the carboy acid (acid III) or out of the strong acid produced in the plant (acid II) finally results in the production of constant-boiling acid that is used in a subsequent decomposition of clay. Distillation of the filtrate from the crystals of aluminum chloride (acid I) yields a solution in the still-pot containing less free acid than the conventional

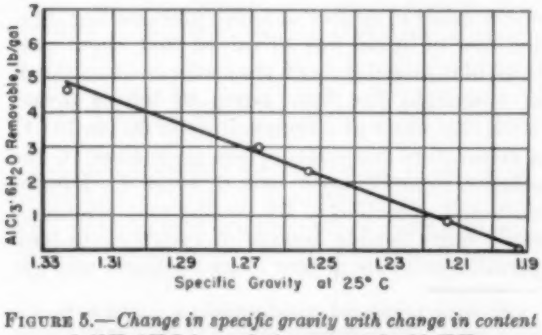

FIGURE 5.—*Change in specific gravity with change in content of $AlCl_3.6H_2O$ in a solution saturated with HCl.*

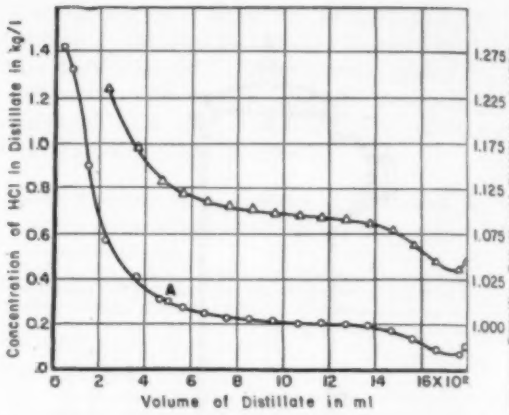

FIGURE 6.—*Distillation of a solution of concentrated hydrochloric acid containing aluminum and iron.*

Δ, specific gravity; o, concentration of hydrochloric acid in distillate; *A*, point where 50 percent of the free HCl was distilled.

constant-boiling hydrochloric acid. This solution contains aluminum chloride and the impurities such as iron, coming from the original clay. After being stripped of its available hydrochloric acid gas, all or part of the residual solution in the still is returned to the digester for the decomposition of more clay. In order to keep the concentration of impurities low enough to produce aluminum chloride of satisfactory purity, a certain percentage of this solution must be removed. To avoid permanent loss of acid, the solution removed at this point is evaporated to dryness, the chloride residue is ignited, the evolved acid is absorbed for reuse, and the final ignited residue is discarded.

TABLE 6.—*Data on precipitation of aluminum chloride*

To produce HCl gas from filtrate from aluminum chloride crystals (acid I, p. 419) requires about 9,000 Btu of HCl gas. About 0.8 lb of HCl gas is obtained from gal of filtrate.

To produce HCl gas from concentrated acid (acid and III, p. 419) requires about 3,500 Btu/lb of HCl g

In operating the plant about one-fourth of the comes from I and about three-fourths from II and Therefore, the average heat consumption in generat gaseous HCl is about 5,000 Btu/lb of HCl gas required

Pounds of HCl gas required to precipitate 1 lb of $AlCl_3.6H_2O$ from concentrated solution	0.5 to 0.
Rate of generating HCl gas, lb/hr	15 to 3
Rate of precipitating $AlCl_3.6H_2O$, lb/hr	35.
Loss of HCl by heating filtrate from aluminum chloride to obtain gas for precipitation, lb HCl gas lost/lb $AlCl_3.6H_2O$ produced in this step	0.188

The amount of solution to be removed to keep the product satisfactory depends on the original soluble impurities in the clay. By far the most important of these is iron.

Figure 6 represents data obtained in the distillation at atmospheric pressure of a typical filtrate from aluminum chloride crystals (I, p. 419). At the beginning of the distillation the solution had the following composition:

Al_2O_3=28.4 g/liter, equivalent to 60.9 g of HCl/liter.
Fe_2O_3=6.8 g/liter, equivalent to 9.3 g of HCl/liter.
Total Cl=347.6 g/liter, equivalent to 351.4 g of HCl/liter.
Free HCl=287.2 g/liter, equivalent to 2.39 lb of HCl/gal.

To obtain these data the usual type of distilling flask was used, and 2 liters of solution were placed in the flask at the start. It is noteworthy that much of the distillate contained less acid than the conventional constant-boiling hydrochloric acid (compare with fig. 3). The slight upturn of the curve at the end of the distillation is caused by decomposition of aluminum chloride as the mass goes to dryness.

Data on precipitation of aluminum chloride are given in table 6.

VIII. Filtration of Aluminum Chloride

From the bottom of the conical tank, figure 4, a 2-inch pipe line led directly to a 20-inch rubber-coated centrifuge with a perforated basket.[15] A valve at the bottom of the tank controlled the flow of the slurry of liquid and crystals to the centrifuge. An asbestos filter cloth was used to retain the crystals in the basket, which holds about 80 lb of aluminum chloride. A slurry containing about 3 lb of aluminum chloride crystals, $AlCl_3.6H_2O$, per gallon filtered quite satisfactorily. In fact, a thick slurry, provided that it flowed freely, gave better performance in the centrifuge than one containing only a few crystals. With a thick slurry, 80 lb of the chloride can easily be obtained in 15 min of centrifuging.

After the basket was full, the crystals were washed with a spray of hydrochloric acid, specific gravity between 1.13 and 1.20. One gallon of acid was sufficient for an 80-lb basket of aluminum chloride, and the washing was completed in less than a minute, with the basket spinning at full speed. The purity of the final product depends largely upon the washing.[16] If alumina of a specially high purity is desired, the amount of washing may be doubled or trebled.

[15] The centrifuge was purchased from Fletcher Works, Philadelphia, Pa.

[16] Microscopical examination of the crystals by Charles Proffer Saylor at the National Bureau of Standards indicates that ferric chloride, which is the chief impurity in the mother liquor, adheres to the surface of the crystal and is not a part of it, even if the solution from which the aluminum chloride is precipitated contains as much as 0.10 lb of ferric oxide, Fe_2O_3, per gal.

X. Conversion of Aluminum Chloride to Aluminum Oxide and Recovery of the Resulting Acid

In preliminary laboratory experiments it was shown that aluminum chloride, $AlCl_3.6H_2O$, can be converted to the oxide by ignition in a muffle furnace or over a free flame at 1,000° C (1,832° F). A gas-fired muffle furnace, having a capacity of 8 cubic feet was installed and used during the first period of operation of the plant, but it was soon realized that ignition of larger quantities of aluminum chloride packed in saggers in a muffle furnace required an excessively long time for satisfactory elimination of chloride and for heating and cooling the furnace. Further laboratory experiments indicated that, if the aluminum chloride could be constantly agitated during ignition, chloride could be eliminated satisfactorily at a lower temperature than that which was necessary in the original muffle furnace. Consequently, the muffle-fired Herreshoff furnace shown in figure 7 was purchased from Nichols Engineering & Research Corporation, New York, N. Y. to replace the original muffle furnace.

In the Herreshoff furnace, the aluminum chloride was constantly agitated by the rabble arms as it passed downward over the heated

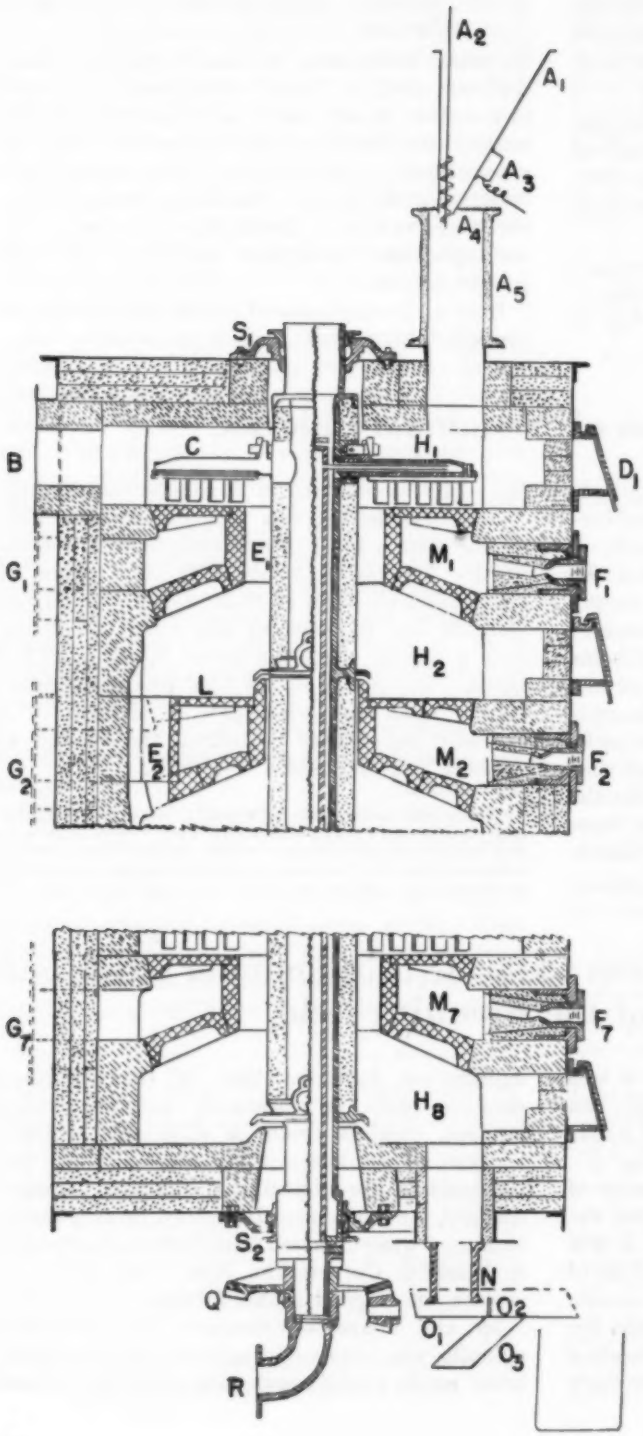

FIGURE 7.—*Muffle-fired Herreshoff furnace.*

A = feeding hopper for the aluminum chloride.
A_2 = a conveyor screw.
A_3 = a Syntron vibrator.
A_4 = an asbestos cloth to prevent escape of gas.
A_5 = a tile pipe.
B = the outlet for the vapors of HCl and water formed by heating $AlCl_3.6H_2O$.
C = a high-silicon rabble arm.
D_1 = an observation port.
E_1 and E_2 = passages to next lower hearths.
F_1, F_2, and F_7 = gas burners.
G_1, G_2, and G_7 = outlets to flue for products of combustion of gas.
H_1, H_2, and H_8 = hearths.
L = "Carbofrax" heat-conducting refractory.
M_1, M_2, and M_7 = muffles.
N = Pyrex glass pipe.
O_1 = delivery chute.
O_2 = a dam to keep alumina at proper level to seal the outlet.
O_3 = a Syntron vibrator.
Q = driving gear.
R = inlet for air to cool shaft and rabble arms.
S_1 and S_2 = seals.

Inside diameter of hearths, 36 in. Effective area of a single hearth, about 825 in.[9]

hearths. The chloride and resulting oxide were never in contact with the products of combustion of the fuel gas.

The muffles of the Herreshoff furnace were made of Carbofrax, the center shaft was made of cast iron covered with acid-proof cement, and most of the exposed metal parts were made of high-silicon iron or other acid-resisting metal. The center shaft and hollow rabble arms were cooled by a forced air current in the conventional way. Attack by the hydrochloric acid gas was not excesssive but was greatest in the upper and cooler portion of the furnace where water and acid condensed. During the operation of both the original muffle and Hereshoff furnaces, the inside of the furnace was maintained at slightly less than atmospheric pressure by the rubber-coated exhaust fan shown in the flow sheet, figure 8, which pulled the water vapor and the hydrochloric acid gas from the top of the furnace through cooler *B*, figure 8, and forced the moist hydrochloric acid gas into the bottom of the absorption tower. After leaving the absorption tower, the gases were forced through the waste tower.

The first and hottest portion of the 4-inch pipe line from the top of the Herreshoff furnace to the cooler was made of Carbofrax pipe; the remainder was made of 4-inch Haveg pipe. As operated, the maximum concentration by volume of hydrochloric acid gas in the 4-inch pipe line between the furnace and the cooler was 12 percent; between the cooler and absorption tower it was 8.0 percent; between the absorption tower and waste tower it was less than 1 percent; and at the exit of the waste tower practically no hydrochloric acid remained. The low concentration of hydrochloric acid gas in the line between the furnace and the cooler indicates that much air was drawn into the system.

Better performance could be obtained with respect to the ratio of hydrochloric acid gas to the other gases in this line if the rate of feed of chloride could be increased, but the absorption system was not adequate for an increased rate of feed.[17] Feeding the aluminum chloride into the top of the furnace presented somewhat of a problem because of the tendency of the crystals to stick together. This stickiness increased in a humid atmosphere. It was found that the chloride could be readily handled if 1 lb of aluminum oxide was mixed with 10 lb of chloride. The final satisfactory equipment for feeding this mixture of chloride and oxide consisted of a hopper equipped with a Syntron vibrator, mounted over the inlet to the furnace. Inside of the hopper was a large vertical motor-driven screw such as is used in screw conveyors. This screw extended into the opening of the furnace. Its speed of rotation determined the rate of feeding of the chloride. When the hopper was kept partly or entirely filled, air did not enter the furnace at the inlet, nor did hydrochloric acid gas escape.

During calcination, finely powdered alumina has a tendency to collect in the gas outlet of the furnace. Provision must therefore be made to remove this dust about once a week to prevent retardation of the gases on their way to the absorbers.

The oxide emerging from the bottom of the furnace was removed by a Syntron vibrating conveyor that was so arranged and regulated that the lower end of the 6-inch glass outlet pipe was always filled with oxide. This prevented air from entering the furnace and diluting the hydrochloric acid gas issuing from the top.

The Herreshoff furnace in which the aluminum chloride was constantly agitated during ignition was far more satisfactory than the ordinary muffle furnace because it made the conversion of chloride

TABLE 7.—*Data on conversion of aluminum chloride to aluminum oxide and recovery of the resulting hydrochloric acid*

Heat required, Btu/lb of $AlCl_3.6H_2O$	4,800
Quantity of condensate, sp gr 1.13 formed (see p. 424), lb/lb of $AlCl_3.6H_2O$	0.45
Quantity of HCl in condensate, lb of HCl/lb of condensate	.27
Quantity of HCl gas obtainable from condensate, lb/lb of chloride	.02
Quantity of HCl in condensate, lb/lb of $AlCl_3.6H_2O$	.12
Total quantity of HCl recovered, lb/lb $AlCl_3.6H_2O$	.41
Total quantity of HCl theoretically recoverable, lb/lb $AlCl_3.6H_2O$	.45
Total HCl lost, lb/lb of $AlCl_3.6H_2O$	.04
Total percentage of HCl recovered in ignition of $AlCl_3.6H_2O$	91.4

Hydrochloric acid gas balance.—A certain amount of hydrochloric acid gas is necessary to maintain the process. Practically all acid lost in the plant escapes as the gas during the precipitation and ignition of aluminum chloride: Carboy acid, sp gr 1.17, was used to make up for losses during operation. By distilling the available hydrochloric acid gas from the makeup acid, a satisfactory gas balance was maintained. Less carboy acid will be required as recovery of the gas from the ignition of chloride is improved. In a large installation the makeup acid could probably be best supplied from salt and sulfuric acid.

[17] The Herreshoff furnace was larger than necessary for the capacity of the rest of the plant. It was purchased as a rebuilt furnace after the other parts of the plant were in operation. At the time of purchase there was no choice as to size and only a limited choice as to design.

to oxide a continuous process and effected elimination of chloride at a lower temperature. The oxide obtained at a minimum of 750° C (1,382° F) in the Herreshoff furnace contained about the same amount of chloride (0.10 to 0.25 percent) as remained in the oxide obtained in the muffle furnace at 950° C (1,742° F) without agitation during ignition.

The ignition of the chloride proceeds according to the equation

$$2AlCl_3.6H_2O + heat = Al_2O_3 + 6HCl + 9H_2O.$$

It is evident that when the gases resulting from this ignition are drawn through the cooler, a certain amount of aqueous hydrochloric acid condenses. This condensate had a specific gravity of about 1.13, and was drained into the Karbate still for later generation of hydrochloric acid gas and decomposition of more clay. The major portion of the hydrochloric acid gas passed through the cooler and was absorbed in cool hydrochloric acid of constant-boiling strength in an absorption tower by the same technic as was used for the precipitation of aluminum chloride (see fig. 4 and description under precipitation of aluminum chloride). In this way the constant-boiling acid was built up to acid of sp gr 1.18 to 1.20 (acid II, p. 419), which was then pumped into the Karbate still and heated to produce hydrochloric acid gas for precipitation of aluminum chloride.

Data on conversion of aluminum chloride to oxide are given in table 7.

X. Properties of the Alumina Produced

The alumina at first obtained in the pilot plant had an average purity of about 99.6 percent. The significant impurities were 0.25 percent of chlorine, 0.04 percent of iron oxide, and 0.06 percent of silica. Spectrochemical tests indicated that the only other impurities were traces of barium, calcium, copper, lithium, magnesium, manganese, and lead. A trace here represents less than 0.01 percent. In more recent calcinations of the aluminum chloride, the resulting alumina had a purity of about 99.8 percent, and contained only 0.1 percent of chlorine, probably because of better operation and better control of the Herreshoff furnace with respect to temperature of hearths and constant rate of feeding. The chloride content can be further reduced by longer heating at higher temperatures. As has already been stated, the content of iron oxide can readily be lowered by additional washing of the chloride in the centrifuge basket if a purer product is desired. In the above, hygroscopic moisture was not regarded as an impurity.

Particle size of the alumina was determined by R. L. Blaine, of the Clay and Silicate Products Division at the National Bureau of Standards. The method of absorption of nitrogen at the temperature of liquid nitrogen described by P. H. Emmet [18] was used, and the values were confirmed by H. F. McMurdie by measurements with an electron microscope. The particles of alumina produced in the Herreshoff furnace had diameters between 0.02 and 0.04 micron. That produced by calcination of aluminum chloride in the original muffle furnace, that is, without rabbling during the ignition, had diameters of about 0.1 micron. This extreme fineness is said to be a disadvantage in the electrolytic reduction of alumina to the metal because of dusting.

The Physical Chemistry Section of the National Bureau of Standards had no particular difficulty from dusting or frothing in an experimental electrolysis in which a slug of 118 g of aluminum metal was produced. A pure graphite crucible served as the cathode, and a pure graphite rod was used as the anode. The electrolyte was molten cryolite. The metal contained 99.5 percent of aluminum, 0.28 percent of iron, and 0.22 percent of silicon. In considering the impurities in this metal, it should be noted that silicon and iron accumulate in the first metal that is reduced, and that pure metal could be obtained on continued electrolysis. The alumina contained 0.03 percent of iron and 0.06 percent of silicon. The cryolite contained about the same percentage of impurities as the alumina.

X-ray examination by H. C. Vacher of the Metallurgical Division of the Bureau showed that the alumina produced by ignition in the Herreshoff furnace at a maximum temperature

[18] A new method for measuring surface areas of finely divide d materials and for determining the size of particles. Symposium on new methods for particle size determination in the sub-sieve range. A. S. T. M. 1941, p. 95 to 105.

of 750° C was γ-alumina; that produced in the muffle by ignition at a temperature of 950° to 1,000° C was α-alumina. The γ-alumina produced in the Herreshoff furnace at 750° C can be converted to α-alumina by heating for 1 hour or more, at or above 1,150° C. The X-ray pattern produced by γ-alumina which had been heated for 5 hours at 1,000° C indicated a partial conversion to the α-form. The results of the X-ray examinations are in approximate agreement with those obtained by M. H. Jellinek and I. Fankuchen [19]

The alumina produced by this process is superior to any alumina on the market at present for polishing certain metallographic specimens. A study of this is being made by G. A. Ellinger.

In the preparation of enamels to be used at high temperatures, W. N. Harrison of the Clay and Silicate Products Division of the Bureau obtained exceptionally satisfactory results with the alumina produced in this pilot plant. The favorable results can probably be attributed to its extreme fineness, rather than to the purity of the alumina.

The alumina produced in the Herreshoff furnace is appreciably hygroscopic. For example, on exposure to the atmosphere it readily absorbs 3 to 4 percent of moisture. If a portion is covered with water and then dried at 110° C, it will retain moisture up to 8 to 10 percent of its original weight. This moisture can again be driven off at 750° C. The resulting ignited oxide will again absorb moisture just as it did originally. This hygroscopicity can be eliminated by ignition at a higher temperature. Such ignition may be necessary if the alumina is to be reduced to metal in the Hall process.

[19] Ind. Eng. Chem. **37**, 158, (1945).

XI. Cost of the Alumina Produced

The cost of construction of a commercial plant for the extraction of alumina from clay is impossible to estimate on the basis of a small pilot plant because the materials of construction used in the two differ very greatly. However, operation of the pilot plant yielded data from which costs of raw materials, heat input, and acid losses can be estimated.

The cost estimates on heat input in table 8 were made on the basis of actual pilot-plant data that were obtained by burning city gas. The gas furnished 600 Btu/ft³, and 2.7 ft³ were assumed to produce 1 lb of steam at 25-lb gage pressure. One pound of this steam released 933 Btu upon condensing. The cost of the city gas was $0.90 per 1,000 ft³. In converting to the basis of coal, it was assumed that the cost of coal was $6.00 a ton, and that 1 lb of coal produced 8 lb of steam. It was further assumed that coal could be burned as efficiently as gas. This last assumption may be rather optimistic, but it is safe to say that in well-insulated furnaces and boilers the efficiency of burning coal is equal to or greater than was actually obtained with gas in the present pilot plant. The steam boiler was insulated, but all the calcining furnaces, stills, and digester were without insulation. On an average, 620 lb of alumina were obtained from 1 ton of kaolin.

TABLE 8.—*Cost estimates on producing alumina*

(a) HEAT INPUT PER TON OF ALUMINA

Steps in process	Btu required	Cost	
		Gas	Coal
Roasting of kaolin	10,900,000	$16.35	$2.51
Digestion of kaolin	5,820,000	15.13	2.34
Concentration of filtrate and washings	82,600,000	214.76	33.20
Formation of HCl gas for precipitation of $AlCl_3.6H_2O$	4,980,000	12.94	2.00
Conversion of $AlCl_3.6H_2O$ to Al_2O_3	45,500,000	68.25	10.46
Total	149,900,000	327.43	50.51

(b) ACID LOSSES

In the calcination of $AlCl_3.6H_2O$, 8.6 percent of the evolved HCl was lost. This was replaced by carboy acid, which cost $0.0235 per lb at the plant.

Cost of acid lost in calcining $AlCl_3.6H_2O$ therefore is	$22.77/ton of Al_2O_3.
Acid lost in producing hydrochloric acid gas by boiling filtrate from aluminum chloride crystals	0.188 lb of HCl/lb of $AlCl_3.6H_2O$ produced in this step.
As only about one-fourth of the gaseous HCl comes from this source, the loss of HCl per ton of Al_2O_3 (500lb×4.74×0.188)=445 lb.	
Carboy acid equivalent of 445 lb of HCl gas	1,270 lb.
Cost of carboy acid at $0.0235/lb	$29.85/ton of Al_2O_3.
Total cost of makeup acid	$52.62/ton of Al_2O_3.

(c) KAOLIN

Cost of kaolin	$5.00/ton of Al_2O_3.

(d) WATER

Cost of cooling water	$1.00/ton of Al_2O_3.
Total cost of producing 1 ton of alumina (exclusive of plant and personnel)	$109.13.

It is evident from the foregoing cost estimates that improvement must be mainly sought in three items, namely, (1) heat required for concentration of filtrate and washings, (2) heat required for conversion of aluminum chloride to the oxide, and (3) acid losses.

With efficient heat exchangers and the utilization of waste heat from furnace gases, the cost of evaporating the filtrate and washings can probably be reduced 75 percent. With insulation of the Herreshoff furnace, the cost of converting aluminum chloride to the oxide can undoubtedly be halved. As the largest item in the tabulation of costs is acid losses, most attention should be given to this. At the time the plant was built, tall absorption towers and acid-proof gas fans were difficult to obtain. Consequently, a certain amount of makeshift equipment was used, which resulted in the losses of acid shown. However, in the manufacture of hydrochloric acid nearly 100 percent of the acid is recovered under similar circumstances. This indicates that the cost of acid losses need not exceed $10.00 per ton of alumina.

With the suggested changes, it is not unreasonable to expect the cost of producing a ton of alumina in the pilot plant to be in the neighborhood of $60.00 a ton on the basis of coal as fuel.

XII. Special Equipment

One of the major problems in constructing a plant in which hydrochloric acid and its salts are to be handled is the procurement and selection of suitable materials of construction. In the descriptive text, mention has been made of tanks, towers, and stills made of Haveg and Karbate for hydrochloric acid solutions at various concentrations and temperatures; of furnaces built of ordinary refractories and with Carbofrax muffles; of ceramic and Carbofrax ducts for hydrochloric acid gas at elevated temperatures; of rubber coated centrifuges for filtering concentrated solutions of hydrochloric acid; of "vinyon resin" filter cloths; of Durichlor pumps for sludges; and of glass pumps for acid solutions. All of these have been satisfactory, but the following supplementary list with comments may serve a useful purpose.

Electric motors.—Three-phase totally enclosed motors have given satisfactory service. A high percentage of failures occurred with unprotected motors exposed to acid fumes or spray. Windings made of glass-coated wire reduced the number of failures.

Pipes.—Haveg, Karbate, chemical stoneware (ceramic), porcelain, glass, and Saran pipe gave satisfactory service. In the present plant Haveg pipe was used in most of the installations because it is easily cut and flanged in any desirable length and is a poor conductor of heat. Karbate likewise can be cut and flanged but is more fragile than Haveg. Karbate with graphite base is used where heat transfer is required. Chemical stoneware pipe lines are satisfactory for certain permanent installations but are fragile, quite heavy and difficult to maintain gas-tight at joints. Porcelain pipes are satisfactory but heavy and expensive. Saran pipe has the desirable quality of being fairly flexible, and it can be "welded" without special equipment. However, it is not recommended for continuous use at temperatures above 170° F. Glass pipe has proved very useful because it enables an operator to follow the progress of reactions. Ordinarily it is not a good conductor of heat, but quite satisfactory heat exchangers can be made of thin-walled glass pipe that is especially made for this purpose.

Valves.—Valves of Haveg, Karbate, stoneware, and porcelain are available and have proved satisfactory. The diaphragms of Haveg and Karbate valves should be made of acid-resistant rubber substitutes.

Pumps.—A Durichlor sludge pump served throughout the entire project for pumping the acid slurry from the digester into the filter press. Examination at the end of 3 years use showed very little acid attack. Glass pumps with graphite packing rings served satisfactorily for pumping all acid solutions. Circulating the solution that was saturated with hydrochloric acid gas and which contained up to 3 lb of aluminum chloride crystals per gallon was the severest test for these pumps. One glass pump was in satisfactory and continuous service for 3 years in such a unit. Stoneware pumps with stuffing boxes were hopelessly unsatisfactory under these conditions. As soon as crystals appeared in the solution, the packing in the

stuffing boxes disappeared so rapidly that repacking was necessary every hour. In general, pumps with stuffing boxes should be avoided in units where strong hydrochloric acid or suspended crystals are involved.

Circulating fans.—Fans made of metal coated with rubber proved to be the most satisfactory for circulating the gases containing hydrochloric acid. Stoneware also gave satisfactory results, although there was a tendency for the acid to penetrate between metal shafts and ceramic impellers, which finally caused failure.

Heat exchangers.—With one exception, all the heat exchangers were made of Karbate with graphite base as the material through which heat was to be transferred. Thin glass pipe previously mentioned was the one exception. Karbate bayonet heaters were used interchangeably for heating and cooling. After heating a solution for a required time with steam, the steam was replaced with cooling water. This arrangement simplified construction.

Stills.—Two stills, one of Haveg the other of Karbate, were in use during the entire project. Both had Karbate bayonet heaters and were about equally satisfactory. Heat losses were greater through the Karbate than through the Haveg.

Waste towers and storage vessels.—Waste towers and storage vessels were made of stoneware.

Gaskets.—Gaskets for flanged pipes were made of Koroseal, (a plasticized polyvinyl chloride). The usual rubber gasket material is unsatisfactory in hydrochloric acid pipe lines because it swells at the flanged junctions and finally nearly seals off small pipes.

Exposed Metal Parts.—In general, exposed metal parts should be painted with acid-resisting paint to prevent corrosion by acid fumes and spray. Small parts may be dipped in hot asphalt. Larger installations can be temporarily protected by painting with such preparations as Bitumastic No. 50 (manufactured by Wailes Dove Hermiston Corporation, Westfield, N. J.).

XIII. Summary and Conclusions

By referring to the flow sheet, figure 8, the steps of the process can be summarized. Words in italics refer to equipment or stages shown on the flow sheet.

Raw *kaolin* enters the *roaster*, then passes to the *digester* containing hot HCl. From the *digester* the slurry goes to the *filter press* where the insoluble matter, consisting largely of SiO_2 *sludge*, is removed and discarded. The acid solution passes to the *still A* where *waste* H_2O is removed, and some dilute hydrochloric acid is thrown back into the "20% HCl *storage*" reservoir, later to be returned to the *digester* for decomposition of more kaolin. From *still A* the concentrated solution goes to the *precipitator* where $AlCl_3.6H_2O$ is precipitated by coming in contact with HCl gas. During saturation with HCl gas the solution is cooled by circulation through *cooler A*. From the *precipitator* the aluminum chloride, suspended in a solution saturated with HCl, goes to the *centrifuge* where the aluminum chloride crystals are removed. From the *centrifuge* the crystals go to the *calciner*, which converts the chloride to the finished product, Al_2O_3, and liberates HCl, part of which condenses in the *cooler B;* the rest is absorbed in the *precipitator* tower after having been cooled in *cooler B*. HCl gas for precipitation of $AlCl_3.6H_2O$ from *still B* is pulled through the *cooler B*, and is circulated through the *precipitator* by the *fan*. The *bleeder valve* serves to regulate recirculation of unabsorbed HCl and to eliminate air and other gases through the *waste tower*. The HCl solutions which are stripped of their gas in *still B* to supply the *precipitator* come from three sources, namely, (1) the filtrate from the *centrifuge*, (2) strong HCl built up in the process, and (3) makeup acid.

After the filtrate from the crystals of aluminum chloride leaves the *centrifuge* and has been stripped of its available HCl gas in *still B*, a part of the residual solution is concentrated to a slurry or cake in the *evaporator*, the dry or nearly dry residue is ignited in the *muffle*, the acid is recovered by absorption, and the solids containing the impurities are discarded as *waste solids*. The remainder of the stripped solution in *still B* goes back into the "20% *storage*" tank for reuse. The amount of the impure residual solution from *still B* that goes to *waste solids* is greater with clays containing large amounts of impurities than with very pure kaolins, and is the means of elminating impurities from the system.

All gases emerging from absorption towers pass through the *waste tower* to catch any unabsorbed gases. The whirling of the *centrifuge* always liberates some HCl gas from the saturated solution. This gas likewise is piped to the *waste tower*.

The process is feasible, but the cost of producing alumina from clay under present conditions is probably 50 percent higher than by the usual Bayer process applied to high-grade bauxite. Installation of efficient heat-exchangers and acid absorption systems will tend to lower costs.

Roasting of kaolin at approximately 700° C renders most of the alumina soluble in dilute acid. It has been shown that the solubility of the alumina in the roasted kaolin is definitely related to the amount of original water of constitution that remains. The more original water that remains, the lower the solubility of the alumina.

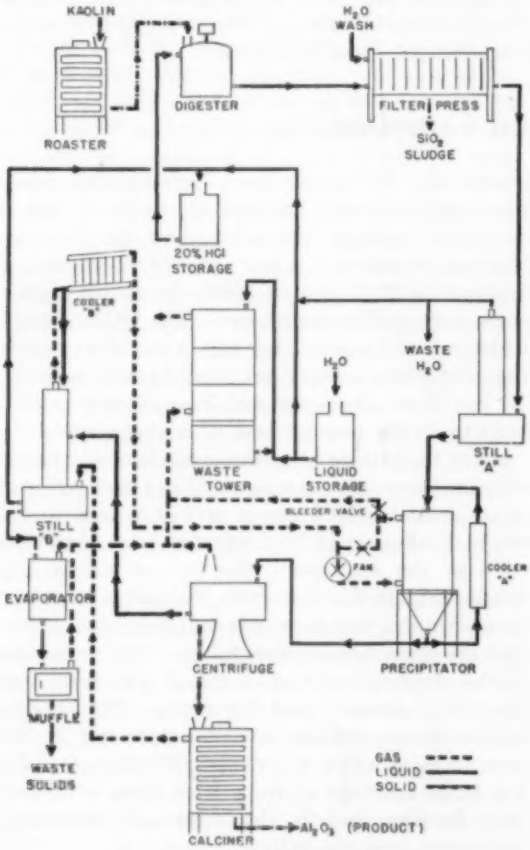

FIGURE 8.—*Detailed flow sheet.*

After proper roasting, the constituents of the kaolin act as if they existed as separate compounds. Silica and titania are practically unattacked by dilute hydrochloric acid; alumina and iron oxide are dissolved, and the heat of reaction corresponds closely to that which should be obtained theoretically by dissolving the same quantity of alumina and iron oxide under the same conditions in the absence of the other constituents of the kaolin.

In the studies on distilling hydrochloric acid solutions containing aluminum chloride, it was found that the final distillates always contained less acid than corresponds to constant-boiling hydrochloric acid. This is true whether the initial acid concentration is greater or less than the constant-boiling acid.

It was found that crystals of aluminum chloride hexahydrate, formed in chloride solutions containing much iron, do not contain any appreciable iron within the crystals. It is therefore possible to remove the iron from the surface of the crystals by thorough washing. This affords an easy control of the iron content of the final product.

Either α-or γ-alumina can be produced by this process by proper control of the temperature of ignition of the chloride to the oxide. All the alumina is extremely finely divided. This may be a disadvantage in the reduction to metallic aluminum because of dusting. It has its advantages, however, if the oxide is to be used as a polishing agent for metallographic specimens, as an ingredient of enamels for service at high temperatures, or in other applications where very finely divided and very pure alumina is desirable.

The authors gratefully acknowledge the service of Raymond L. Dodson, who conducted experiments on the decomposition of clays in the early stages of the project; of Wilmer A. Hemminger, who conducted most of the roasting operations in the latter stages of the project; of Willard D. Hubbard, who was responsible for the precipitation cycle and for the calculations on heat transfer and material balances; of George A. Derbyshire, who assisted in the large-scale decomposition of clay near the end of the project; and of Herbert B. Lowey, whose assistance in the mechanical construction of the plant was a notable factor in its successful operation.

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Study of Ofner's Method for the Determination of Invert Sugar

By Emma J. McDonald and Anne L. Turcotte

In a previous investigation Jackson and McDonald studied Ofner's method for the determination of invert sugar in sucrose. They modified the procedure and were thus able to increase the reproducibility of results when determining from 5 to 25 mg of invert sugar in the presence of sucrose. This method has now been applied to pure invert sugar and to sugar samples containing 5 mg or less of invert sugar in 10 g of sucrose. It has proved to be a suitable method for the analysis of high-grade refined sugars as well as for the determination of 25 mg or less of invert sugar alone. A table is given for the conversion of milliliters of iodine consumed to milligrams of invert sugar present.

I. Introduction

It has long been recognized that copper solutions of low alkalinity are better suited for the analysis of small amounts of invert sugar in the presence of sucrose than are those of higher alkalinity. The method devised by Ofner [1][1] for the determination of invert sugar in refined sugars has been subjected to critical study by Jackson and McDonald [2]. These authors recommended the use of the Ofner method with some modifications. These included the substitution of an ordinary asbestos gauze plate for the metal gauze, thus insuring more uniform heating and the elimination of the "flame spot." The precision of the method was greatly increased by acidifying with acetic acid before the addition of iodine and subsequent addition of hydrochloric acid. Thus, the rapid oxidation of cuprous chloride in acid solution was eliminated.

Jackson and McDonald confined their experiments to sugar samples containing from 5 to 25 mg of invert sugar, which amounts to 0.05 to 0.25 percent when a 10-g sample is used. In the present investigation the precision of the method was determined with invert sugar alone, and with sugar samples containing less than 0.05 percent of invert sugar. The results further confirm the validity of the modified Ofner method for the analysis of refined sugars.

Experience has shown that invert sugar can be determined more accurately alone than when in the presence of sucrose. Therefore, it seemed advisable to base the results on the invert-sugar values and to apply a correction for the increased reduction due to the action of the sucrose.

[1] Figures in brackets indicate the literature references at the end of this paper.

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II. Analytical Procedure

Invert sugar used in these experiments was prepared by weighing equal quantities of levulose and dextrose and by the hydrolysis of pure sucrose. Identical analytical results were obtained from invert sugar prepared by the two procedures. The sucrose and dextrose used were National Bureau of Standards Standard Samples 17 and 41, respectively; the levulose was purified by repeated crystallization from aqueous alcohol solution. Iodine of a normality of 0.0323 was used except when 5 mg or less of invert sugar was de termined, in which case 0.00323 *N* iodine was em ployed. All results were expressed in terms o the 0.0323 *N* solution. The concentration of th iodine solution was determined by volumetri titration against thiosulfate of the same norma ity. The thiosulfate solution was repeatedl standardized [3, 4] against pure copper or a copp sulfate solution in which the copper had bee determined electrolytically.

1. Method

(a) Reagents

Copper solution.—Dissolve 5.0 g of $CuSO_4.5H_2O$, 10.0 g of anhydrous Na_2CO_3, 300 g of pulverized Rochelle salt, and 50 g of $Na_2HPO_4.12H_2O$, or 19.8 g of anhydrous salt in about 900 ml of water, warming finally if necessary. When these reagents are completely dissolved, it is advisable to continue heating for 2 hours on the water bath to destroy mold spores. Cool, and adjust the volume to 1 liter. Treat with active carbon or kieselguhr and filter, or filter directly through sintered glass having fine pores. Preserve in a dark place.

Sodium thiosulfate solution.—Dissolve 4.00 g of crystals and dilute to a volume of 500 ml or, preferably, prepare a stock solution containing in 500 ml, 20.0 g of crystals and 1 ml of 1 *N* NaOH or 0.1 g of Na_2CO_3. Dilute 100 ml of this stock solution to 500 ml as required. Standardize by titration against pure copper solution.

Iodine solution.—Dissolve 2.05 g of pure iodine in about 10 g of iodate-free KI dissolved in a few milliliters of water. Dilute to a volume of exactly 500 ml and preserve in a dark place. This solution is 0.03230 *N*. It is repeatedly standardized against copper by means of the thiosulfate.

Starch solution.—Rub 2.5 g of soluble starch and about 10 mg of HgI_2 in a little water. Dissolve i about 500 ml of boiling water.

(b) Procedure

Dissolve a 20-g sample of the sugar in distille water and dilute to 100 ml. Transfer 50 ml the solution containing not more than 20 mg invert sugar to a 300-ml Erlenmeyer flask and ad 50 ml of the copper reagent. Mix well, add 50 100 mg of pumice or talcum powder, cover wit a glass bulb or inverted beaker, and heat t boiling on an absestos gauze plate during 4 to minutes. Judge the initial time of boiling, n when bubbles arise from the bottom of the flas but when they burst at the surface in conside able number. Continue the boiling for exact 5 minutes. Cool without agitation by immersio in cold tap water. Add 1 ml of glacial acetic aci Add with continuous agitation an accurate measured volume of iodine, 5 to 30 ml, accordin to the amount of copper reduced, so that an exce is finally present. Pour down the wall of the fla from a graduated cylinder 15 ml of 1 *N* HC Stopper the flask and allow the iodine to react f about 2 minutes, occasionally agitating the sol tion. Titrate the excess iodine with thiosulfat with the addition of starch as the end point approached.

III. Reducing Power of Invert Sugar

Forty-five analyses were made in which quantities of invert sugar varying from 0.5 to 25 mg were determined. The data were treated by the method of averages in order to obtain a mathematical relation between the iodine consumed and the invert sugar present. It was found than when not more than 5 mg of invert sugar was present, the following linear relation existed:

$$S=0.177+1.0124\ I, \qquad (1)$$

where S=milligrams of invert sugar, and I=milliliters of 0.0323 N iodine consumed. Above this range the following quadratic equation was found to apply:

$$S=0.817+0.855\ I+0.005117\ I^2 \qquad (2)$$

Table 1 records a series of determinations of known quantities of invert sugar, in which the sugar is calculated from the iodine consumed by means of equation 1 or 2.

Ofner found that 1 ml of 0.0323 N iodine was equivalent to 1 mg of invert sugar. The changes in the procedure, however, make the results more reproducible, and thus the analytical results warrant the more precise mathematical treatment. Table 2 correlates the iodine consumed and the invert sugar present. It is calculated by means of the above equations and is intended for practical application.

TABLE 1.—*Determination of invert sugar*

0.0323 N iodine	Invert sugar			0.0323 N iodine	Invert sugar		
	Present	Determined from I_1 consumed by means of equation 1 or 2	Difference		Present	Determined from I_2 consumed by means of equation 1 or 2	Difference
ml	*mg*	*mg*	*mg*	*ml*	*mg*	*mg*	*mg*
0.33	0.5	[a]0.5	0.0	19.94	10.0	9.8	−0.2
.51	.7	.7	.0	12.62	12.5	12.4	−.1
.82	1.0	1.0	.0	12.71	12.5	12.5	.0
.81	1.0	1.0	.0	12.72	12.5	12.5	.0
1.27	1.5	1.5	.0	12.59	12.5	12.4	−.1
1.75	2.0	2.0	.0	12.55	12.5	12.35	−.15
1.76	2.0	2.0	.0	15.14	15.0	14.9	−.1
1.76	2.0	2.0	.0	15.52	15.0	15.3	+.3
2.21	2.5	2.4	−.1	15.00	15.0	14.8	−.2
2.75	3.0	3.0	.0	15.29	15.0	15.1	+.1
2.78	3.0	3.0	.0	17.18	16.9	17.0	+.1
3.01	3.4	3.2	−.2	17.63	17.5	17.5	.0
3.80	4.0	3.9	−.1	17.47	17.5	17.3	−.2
3.86	4.0	4.1	+.1	20.04	20.0	20.0	.0
4.05	4.4	4.3	−.1	19.85	20.0	19.8	−.2
4.90	5.0	5.1	+.1	20.11	20.0	20.1	+.1
4.94	5.0	5.2	+.2	22.52	22.5	22.7	+.2
4.93	5.0	[b]5.2	+.2	22.40	22.5	22.5	.0
7.46	7.5	7.5	.0	22.31	22.5	22.4	−.1
7.48	7.5	7.5	.0	24.52	25.0	24.9	−.1
7.43	7.5	7.45	−.05	24.85	25.0	25.2	+.2
10.01	10.0	9.9	−.1	24.72	25.0	25.1	+.2
10.09	10.0	10.0	.0				

[a] The first 17 values under this heading were calculated by the equation $S=0.177+1.0124\ I$, where S=milligrams of invert sugar, and I=milliliters of 0.0323 N iodine consumed.

[b] The last 28 values under this heading were calculated by the equation $S=0.817+0.855\ I+0.005117\ I^2$, where S=milligrams of invert sugar, and I=milliliters of 0.0323 N iodine consumed.

TABLE 2.—*Iodine-invert sugar equivalents*

0.0323 *N* iodine	Fractional milliliters of 0.0323 *N* iodine									
	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	Milligrams of invert sugar									
ml										
0				0.48	0.58	0.68	0.78	0.89	0.99	1.09
1	1.19	1.29	1.39	1.49	1.59	1.70	1.80	1.90	2.00	2.10
2	2.20	2.30	2.40	2.51	2.61	2.71	2.81	2.91	3.01	3.11
3	3.21	3.31	3.41	3.52	3.62	3.72	3.82	3.92	4.02	4.12
4	4.23	4.33	4.43	4.53	4.63	4.73	4.83	4.94	5.04	5.14
5	5.24	5.33	5.41	5.50	5.59	5.67	5.77	5.86	5.95	6.04
6	6.13	6.22	6.32	6.41	6.50	6.59	6.68	6.78	6.87	6.96
7	7.05	7.15	7.24	7.33	7.43	7.52	7.61	7.70	7.80	7.89
8	7.98	8.08	8.17	8.27	8.36	8.45	8.55	8.64	8.74	8.83
9	8.93	9.02	9.12	9.21	9.31	9.40	9.50	9.59	9.69	9.79
10	9.88	9.98	10.07	10.17	10.26	10.36	10.45	10.55	10.65	10.74
11	10.84	10.94	11.03	11.13	11.23	11.33	11.42	11.52	11.62	11.71
12	11.81	11.91	12.01	12.11	12.21	12.30	12.40	12.50	12.60	12.70
13	12.80	12.90	12.99	13.09	13.19	13.29	13.39	13.49	13.59	13.69
14	13.79	13.89	13.99	14.09	14.19	14.29	14.39	14.49	14.59	14.69
15	14.79	14.89	14.99	15.10	15.20	15.30	15.40	15.50	15.60	15.71
16	15.81	15.91	16.01	16.11	16.21	16.32	16.42	16.52	16.63	16.73
17	16.83	16.93	17.04	17.14	17.24	17.35	17.45	17.55	17.66	17.76
18	17.86	17.97	18.07	18.18	18.28	18.39	18.49	18.60	18.70	18.81
19	18.91	19.01	19.12	19.22	19.33	19.44	19.54	19.65	19.75	19.86
20	19.96	20.07	20.18	20.28	20.39	20.49	20.60	20.71	20.81	20.92
21	21.03	21.14	21.24	21.35	21.46	21.56	21.67	21.78	21.89	22.00
22	22.10	22.21	22.32	22.43	22.54	22.64	22.75	22.86	22.97	23.08
23	23.19	23.30	23.41	23.52	23.62	23.73	23.84	23.96	24.07	24.18
24	24.28	24.39	24.50	24.61	24.72	24.83	24.95	25.06	25.17	25.28

IV. Effect of Sucrose on the Reducing Power of Invert Sugar

It has been shown by many investigators that sucrose, even after careful purification, has a reducing effect on alkaline copper solutions. Thus, in using any method employing these reagents, the question arises whether to make a correction for the reduction of pure sucrose or to express the results on the basis of invert sugar alone. If a correction is to be made, the reducing power of very pure sucrose must be determined. Bates and Jackson [5], using Soldaini's reagent (a copper carbonate-bicarbonate solution), found a reduction of copper corresponding to 0.006 percent invert sugar content in pure sucrose. Kraisy, using a copper carbonate tartrate solution, found 0.007 percent, while Sandera and Merceo, and the New York Sugar Trade Laboratory, using the same method [6], found 0.003 percent as the invert content of sucrose. Ofner reports that 10 g of sucrose reduces copper equivalent to 1 ml of 0.0323 *N* iodine, or 0.01 percent invert sugar. Jackson and McDonald [2] found that 10 g of sucrose reduced copper equivalent to 1.1 ml of 0.0323 *N* iodine but did not determine the pure invert sugar equivalent. In the present investigation it has been found that the reducing power of 10 g of a National Bureau of Standards Standard Sample of Sucrose is equivalent to 1.1 ml of iodine or 0.013 percent of invert sugar.[3]

If the sucrose hydrolyzes during the determination, it would be expected that methods employing different boiling times and solutions varying in pH would give varying results. It is known that the alkaline solutions, such as Soxhlet's, have a hydrolytic effect on sucrose, and for this reason they are not adaptable to the determination of

[3] Repeatedly recrystallized and freshly prepared sucrose samples occasionally gave values as low as 0.006 percent of invert sugar when analyzed by this method.

refined sugars. A series of analyses was made in which 1 mg of invert sugar and a sample of sucrose containing 1.3 mg of apparent invert sugar was determined by the method under consideration, using 1 to 20 minutes of boiling time. The results are shown in figure 1. It is concluded from the difference in the slopes of the curves at the 5-

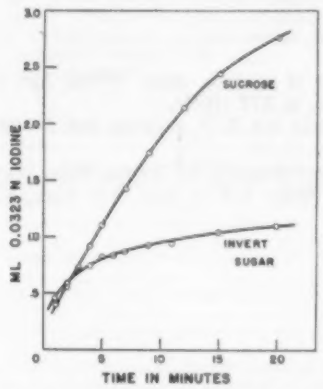

FIGURE 1.—*Effect of the time of boiling on the determination of invert sugar and sucrose.*

minute boiling time (the conditions specified in the method) that the reducing effect of sucrose is caused, at least in part, by substances formed during the analysis rather than those in the original sample. These results also show that when sucrose is present, small variations in the boiling time will have a greater effect on the amount of copper reduced than when invert sugar alone is present.

Many investigators, using different copper solutions under varying conditions, have studied the effect of sucrose on the reducing power of invert sugar. Ofner reported that, irrespective of the relative amounts of sucrose and invert sugar present, 10 g of the former or 1 mg of the latter reduced copper equivalent to 1 ml of 0.0323 *N* iodine.

In table 3 the results of the analyses of seven samples of sucrose, alone and with known amounts of added invert sugar, are tabulated. It was found that when the total invert sugar content of 10 g of sucrose was not more than about 5 mg, the effect of the sucrose and added invert sugar seemed to be additive. It is therefore recommended that for sucrose samples containing 0.05 percent or less of invert sugar the iodine used be converted to invert sugar by the use of table 2. The results thus obtained may be reported as apparent invert sugar, or a correction amounting to 1.1 ml of 0.0323 *N* iodine for each 10-g sample of sucrose may be subtracted in order to compensate for the reduction of pure sucrose. In the latter case the results would be expressed as invert sugar and would not include the apparent invert sugar caused by the reducing action of the pure sucrose.

For amounts of invert sugar above 5 mg, the table published by Jackson and McDonald [2] is more convenient and accurate.

TABLE 3.—*Reducing power of sucrose alone and with added invert sugar*

Sugar sample	10 g of sucrose		Milligrams of invert sugar added									
	Is	Invert sugar by formula	1		2		3		4		5	
			Present	Found	Present	Found	Present	Found	Present	Found	Present	Found
	ml	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
	1.61	1.8	2.8	2.8	3.8	3.4	4.8	4.6	5.8	5.9	6.8	7.2
	1.07	1.3	2.3	2.3			4.3	4.4	5.3	5.5	6.3	6.5
	1.71	1.9	2.9	2.9	3.9	3.8	4.9	5.1	5.9	6.0	6.9	7.2
	1.07	1.3	2.3	2.3	3.3	3.3	4.3	4.2	5.3	5.3		
	1.66	1.9	2.9	2.8	3.9	3.4	4.9	4.6	5.9	5.9	6.9	7.2
	1.06	1.25	2.25	2.2	3.25	3.25	4.25	4.3	5.25	5.4	6.25	6.6
	5.98	6.2	7.2	7.2	8.2	8.4	9.2	9.6				

V. Summary and Conclusions

Ofner's method, as modified by Jackson and McDonald, has been used for the determination of invert sugar, and a table giving the invert-sugar equivalents of the iodine consumed has been prepared. It has been shown that this is a convenient and reliable method for the analysis of high-grade refined sugars.

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